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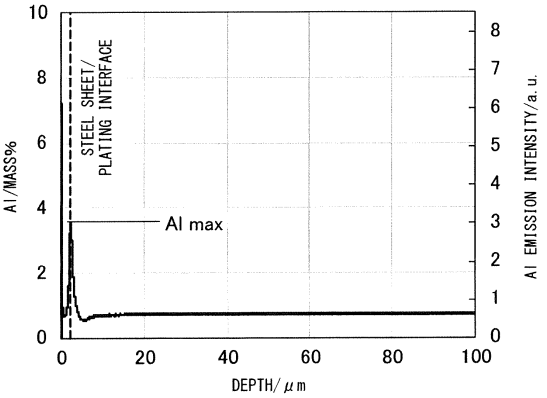
(54) HOT-DIP GALVANIZED STEEL SHEET AND METHOD FOR PRODUCING SAME

(57) Provided are a hot dip galvanized steel sheet having a predetermined chemical composition, and a steel microstructure comprising, by vol%, ferrite: 0 to 50%, tempered martensite: 1% or more, retained austenite: 5% or more, fresh martensite: 0 to 15%, total of pearlite and cementite: 0 to 5%, and balance: bainite, when measuring by GDS, a maximum value of Al concentration of an Al rich layer present at an interface of the base steel sheet and the hot dip galvanized layer is 2.0 mass% or more and an Si_s/Si_b right under the interface is 0.90 or less, a number density of recessed parts with a depth of more than 2 μm at the interface is 2.0/100 μm or less per interface length, and a tensile strength is 980 MPa or more, and a method for producing the same.

Fig. 3



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Description

FIELD

[0001] The present invention relates to a hot dip galvanized steel sheet and a method for producing the same, more particularly relates to a high strength hot dip galvanized steel sheet mainly used as steel sheet for automotive use and a method for producing the same.

BACKGROUND

[0002] In recent years, improvement has been sought in the fuel efficiency of automobiles from the viewpoint of restrictions on emission of greenhouse effect gases accompanying measures against global warming. A high strength steel sheet is being increasingly applied so as to lighten the weight of vehicle bodies and secure collision safety. In particular, recently, there has been an increasing need for a high strength steel sheet with a tensile strength of 980 MPa or more. Further, in vehicle bodies as well, a high strength hot dip galvanized steel sheet which is hot dip galvanized at its surface is sought for portions where rust resistance is demanded.

[0003] The steel sheet used for automobile members require not only strength, but also press-formability and weldability and other types of processability required for forming parts. Specifically, from the viewpoint of press-formability, a steel sheet is being asked to provide excellent elongation (total elongation EL at tensile test) and stretch flangeability (hole expansion ratio: λ).

[0004] In general, along with the higher strength of a steel sheet, the press-formability becomes worse. As means for achieving both higher strength and press-formability of steel sheet, TRIP (transformation induced plasticity) steel sheet utilizing the transformation induced plasticity of retained austenite is known.

[0005] PTLs 1 to 3 disclose high strength TRIP steel sheet with percentages of microstructure components controlled to predetermined ranges and improved in elongation and hole expansion ratio. Further, PTL 4 describes a high strength steel sheet having a predetermined chemical composition, comprising ferrite with an average crystal grain size of 2 μm or less in a volume percentage of 15% or less, retained austenite with an average crystal grain size of 2 μm or less in a volume percentage of 2 to 15%, martensite with an average crystal grain size of 3 μm or less in a volume percentage of 10% or less, and a balance of bainite and tempered martensite with an average crystal grain size of 6 μm or less, and containing an average of 10 or more cementite particles with a grain size of 0.04 μm or more in the bainite and tempered martensite grains and described that the high strength steel sheet has a 1180 MPa or more tensile strength and has high elongation and hole expandability and an accompanying excellent bendability.

[0006] PTL 5 discloses TRIP steel sheet improved in stretch flangeability by limiting the area ratio of blocky (low aspect ratio) retained austenite.

[0007] PTL 6 discloses high strength TRIP steel sheet large in work hardening in initial shaping and having excellent shape freezeability and workability by control of the amount of dissolved Si and amount of dissolved Mn contained in the retained austenite to predetermined values or more.

[0008] Further, a steel sheet for automotive use is asked to provide excellent weldability in addition to press-formability. In particular, in the welding of hot dip galvanized steel sheets with each other or the welding of a hot dip galvanized steel sheet and nonplated steel sheet, liquid metal embrittlement (LME) cracking has to be suppressed. This phenomenon is cracking arising due to action of the tensile stress generated by the welding at places where zinc rendered a liquid phase due to the weld heat input penetrates inside the steel sheet along the grain boundaries and causes embrittlement.

[0009] The fact that LME cracking occurs more easily the greater the amount of Si contained in the steel is disclosed in PTL 7. Therefore, that document discloses TRIP steel sheet in which, instead of part of the Si added to obtain retained austenite in TRIP steel, Al having a similar effect is added. Further, TRIP steel sheet in which Al is added in place of part of the Si is disclosed in PTLs 8 and 9 as well.

[0010] Further, PTL 10 discloses a method of production of a hot dip galvanized steel sheet excellent in LME cracking resistance characterized by controlling the atmosphere at the time of heating and annealing at the hot dip galvanization line.

[CITATIONS LIST]

[PATENT LITERATURE]

[0011]

[PTL 1] WO 2013/051238
[PTL 2] Japanese Unexamined Patent Publication No. 2006-104532

[PTL 3] Japanese Unexamined Patent Publication No. 2011-184757
[PTL 4] WO 2017/179372
[PTL 5] WO 2018/190416
[PTL 6] WO 2013/018741
[PTL 7] WO 2018/202916
[PTL 8] Japanese Unexamined Patent Publication No. 2011-17046
[PTL 9] WO 2013/144377
[PTL 10] WO 2018/234938

SUMMARY

[TECHNICAL PROBLEM]

[0012] In this field, there is an ongoing need for a hot dip galvanized steel sheet achieving both higher strength and press-formability while being excellent in LME cracking resistance. In the steel sheet or hot dip galvanized steel sheet of the prior art, there remains room for improvement from these viewpoints.

[0013] Therefore, an object of the present invention is to provide a hot dip galvanized steel sheet excellent in press-formability and LME cracking resistance of spot welds and a method for producing the same.

[SOLUTION TO PROBLEM]

[0014] The inventors engaged in intensive studies for achieving the above object and as a result discovered that the sensitivity of spot welds to LME cracking in a hot dip galvanized steel sheet is remarkably improved in the following cases.

Case where interface of the base steel sheet and hot dip galvanized layer is smooth

[0015] Recessed parts present at the interface of the base steel sheet and hot dip galvanized layer (below, also simply referred to as the "steel sheet/plating interface") easily accumulate Zn melted by the input heat at the time of spot welding and become parts where stress concentrates, and therefore it is believed that easily become starting points of LME cracking. In the present invention, it is not the recessed/projecting parts of the hot dip galvanized steel sheet, but the recessed parts of the steel sheet/plating interface that are important. This feature fundamentally differs from the generally measured steel sheet roughness. Specifically, the inventors discovered that if the number density of recessed parts with depths at the steel sheet/plating interface of more than 2 μm is 2.0/100 μm or less per interface length, a remarkable effect of improvement is obtained.

Case where Al concentration of Al rich layer present at steel sheet/plating interface is high

[0016] The detailed mechanism is not clear, but it is believed there is a possibility that the Al rich layer present at the steel sheet/plating interface inhibits the penetration of molten Zn into the base steel sheet. Further, the inventors discovered that this effect becomes larger the higher the Al concentration in the Al rich layer. Specifically, the inventors discovered that if the maximum value of the Al concentration of the Al rich layer present at the steel sheet/plating interface is 2.0 mass% or more when using a high frequency glow discharge optical emission spectrometer (GDS) to measure the Al concentration from the surface of the hot dip galvanized steel sheet down in the depth direction, a remarkable effect of improvement is obtained.

Case where low Si layer (Si poor layer) is present at base steel sheet right below steel sheet/plating interface

[0017] This is believed to be because Si is an element causing the LME cracking sensitivity to worsen, therefore if the Si concentration at the region of the base steel sheet right below the plating interface contiguous with the molten Zn is low, the LME cracking sensitivity is improved. Specifically, the inventors discovered that if the Si_s/Si_b at the base steel sheet right under the steel sheet/plating interface is 0.90 or less when using a high frequency glow discharge optical emission spectrometer (GDS) to measure the emission intensity of Si from the surface of the hot dip galvanized steel sheet down in the depth direction, a remarkable effect of improvement is obtained.

[0018] The present invention was realized based on the above discoveries and specifically is as follows:

(1) A hot dip galvanized steel sheet comprising a base steel sheet and a hot dip galvanized layer formed on at least one surface of the base steel sheet, wherein the base steel sheet has a chemical composition comprising, by mass%,

C: 0.15 to 0.30%,
Si: 0.30 to 2.50%,
Mn: 1.40 to 3.49%,
P: 0.050% or less,
S: 0.0100% or less,
Al: 0.001 to 1.50%,
N: 0.0100% or less,
O: 0.0100% or less,
Cr: 0 to 1.00%,
Mo: 0 to 1.00%,
Cu: 0 to 1.00%,
Ni: 0 to 1.00%,
Co: 0 to 1.00%,
W: 0 to 1.00%,
Sn: 0 to 1.00%,
Sb: 0 to 0.50%,
Nb: 0 to 0.200%,
Ti: 0 to 0.200%,
V: 0 to 1.00%,
B: 0 to 0.0050%,
Ca: 0 to 0.0100%,
Mg: 0 to 0.0100%,
Ce: 0 to 0.0150%,
Zr: 0 to 0.0100%,
La: 0 to 0.0150%,
Hf: 0 to 0.0100%,
Bi: 0 to 0.0100%,
REM other than Ce and La: 0 to 0.0100% and
balance: Fe and impurities, and
a steel microstructure in a range of 1/8 thickness to 3/8 thickness centered on 1/4 thickness from the surface of the base steel sheet comprising, by vol%,
ferrite: 0 to 50%,
tempered martensite: 1% or more,
retained austenite: 5% or more,
fresh martensite: 0 to 15%,
total of pearlite and cementite: 0 to 5%, and
balance: bainite,
when measuring the hot dip galvanized steel sheet by a high frequency glow discharge optical emission spectrometer (GDS), a maximum value of Al concentration of an Al rich layer present at an interface of the base steel sheet and the hot dip galvanized layer is 2.0 mass% or more and an Si_s/Si_b at the base steel sheet right under the interface of the base steel sheet and the hot dip galvanized layer is 0.90 or less,
a number density of recessed parts with a depth of more than 2 μm at the interface of the base steel sheet and the hot dip galvanized layer is 2.0/100 μm or less per interface length, and a tensile strength is 980 MPa or more, where

Si_s : local minimum value of Si emission intensity at base steel sheet right under interface of base steel sheet and hot dip galvanized layer
Si_b : average value of Si emission intensity at base steel sheet.

(2) The hot dip galvanized steel sheet according to (1), wherein the chemical composition comprises, by mass%,

Si: 0.30 to 1.20% and
Al: 0.30 to 1.50%.

(3) A method for producing the hot dip galvanized steel sheet according to (1) or (2), comprising

(A) a hot rolling step including hot rolling a slab having the chemical composition according to (1) or (2), then coiling and cooling the obtained hot rolled steel sheet, wherein the cooling satisfies the following formula (1):

[Mathematical 1]

$$0.05 < \sqrt{2 \cdot \sum_{t=0}^{tf} \left(\frac{Do \cdot No}{N_x} \cdot \Delta t \right)} < 1.50 \quad \cdots \ (1)$$

where,
[Mathematical 2]

$$D_o = 2.9 \cdot 10^{-7} \cdot exp\left(-\frac{90{,}000}{8.314 \cdot T(t)} \right) \quad \cdots \ (2)$$

[Mathematical 3]

$$N_o = 0.381 \cdot exp\left(-\frac{104{,}000}{8.314 \cdot T(t)} \right) \quad \cdots \ (3)$$

T(t): steel sheet temperature (K) after elapse of "t" seconds from coiling
tf: time (s) until steel sheet temperature reaches 673K
Nx: total of atomic percents (-) of Si, Mn, and Al in steel

(B) a pickling step including applying at least one bending/unbending deformation to the hot rolled steel sheet, then running the hot rolled steel sheet through a temperature 70 to 90°C aqueous solution containing 1.0 to 5.0 mol/L of HCl, less than 3.0 mol/L of Fe^{2+}, and less than 0.10 mol/L of Fe^{3+} by an average speed of 10 m/min or more as pickling treatment for 30 seconds or more,
(C) a cold rolling step of cold rolling the hot rolled steel sheet after the pickling treatment by a rolling reduction of 30 to 75%,
(D) a heat treatment and plating step including heat treating and plating the obtained cold rolled steel sheet, wherein the heat treatment and plating step satisfies the conditions of the following (D1) to (D4)

(D1) heating the cold rolled steel sheet to give an average heating speed from 600°C to an Ac1+30°C to 950°C maximum heating temperature of 0.2 to 20°C/s, wherein an atmosphere around the cold rolled steel sheet satisfies the following formula (4):
[Mathematical 4]

$$-1.0 < \log\left(\frac{pH_2O}{pH_2} \right) < -0.1 \quad \cdots \ (4)$$

pH_2O: steam partial pressure
pH_2: hydrogen partial pressure

(D2) holding the cold rolled steel sheet at the maximum heating temperature for 1 to 1000 seconds,
(D3) the time after dipping in the plating bath until gas wiping is 0.1 to 5 seconds and the steel sheet temperature after gas wiping is 440°C or less, and
(D4) cooling the steel sheet to a range of Ms to Ms-200°C, then reheating to a temperature region of 300 to 420°C and holding at the temperature region for 100 to 600 seconds.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0019] According to the present invention, it is possible to obtain a hot dip galvanized steel sheet excellent in press-formability and LME cracking resistance of spot welds.

BRIEF DESCRIPTION OF DRAWINGS

[0020]

FIG. 1 is a view for explaining a method for measuring a number density of recessed parts with a depth of more than 2 μm at an interface of a base steel sheet and hot dip galvanized layer.
FIG. 2 is a view for explaining a method for measuring a maximum value of an Al concentration of an Al rich layer present at an interface of a base steel sheet and hot dip galvanized layer.
FIG. 3 is a view for explaining a method for measuring a maximum value of an Al concentration of an Al rich layer present at an interface of a base steel sheet and hot dip galvanized layer.
FIG. 4 is a view for explaining a method for measuring Si_s /Si_b at a base steel sheet right under an interface of a base steel sheet and hot dip galvanized layer.

DESCRIPTION OF EMBODIMENTS

"Chemical Composition of Base Steel Sheet"

[0021] First, the reasons for limiting the chemical composition of the base steel sheet according to an embodiment of the present invention (below, also simply referred to as the "steel sheet") in the above way will be explained. In this Description, the "%"'s defining the chemical composition are all "mass%" unless particularly indicated otherwise. Further, in this Description, the "to" showing a numerical range is used in a sense including the numerical values described before and after it as an upper limit value and a lower limit value unless particularly indicated otherwise.

[C: 0.15 to 0.30%]

[0022] C (carbon) is an element essential for securing the strength of steel sheet. To sufficiently obtain such an effect, the C content is 0.15% or more. The C content may also be 0.16% or more, 0.18% or more, or 0.20% or more. On the other hand, if excessively including C, the press-formability and other workability and the weldability will sometimes decline. For this reason, the C content is 0.30% or less. The C content may also be 0.28% or less, 0.27% or less, or 0.25% or less.

[Si: 0.30 to 2.50%]

[0023] Si (silicon) is an element suppressing the formation of iron carbides and contributing to improvement of the strength and shapeability. To sufficiently obtain these effects, the Si content is 0.30% or more. The Si content may also be 0.40% or more, 0.50% or more, 0.51% or more, 0.52% or more, 0.55% or more, 0.60% or more, or 0.70% or more. On the other hand, excessive addition sometimes aggravates the LME cracking at the time of welding. Therefore, the Si content is 2.50% or less. From the viewpoint of suppressing LME cracking, the Si content is preferably lower. Specifically, 2.00% or less is preferable, and 1.50% or less is more preferable. In particular, if limiting the Si content to 1.20% or less, it is possible to obtain particularly excellent LME cracking sensitivity resistance.

[Mn: 1.40 to 3.49%]

[0024] Mn (manganese) is a powerful austenite stabilizing element and an element effective for raising the strength of steel sheet. To sufficiently obtain such an effect, the Mn content is 1.40% or more. The Mn content may be 1.50% or more, 1.70% or more, or 2.00% or more. On the other hand, excessive addition sometimes causes deterioration of the press-formability and other workability and the weldability and furthermore the low temperature toughness. Therefore, the Mn content is 3.49% or less. The Mn content may also be 3.20% or less, 3.00% or less, or 2.90% or less.

[P: 0.050% or Less]

[0025] P (phosphorus) is a solution strengthening element and an element effective for making the steel sheet high strength, but excessive addition causes deterioration of the weldability and toughness. Therefore, the P content is limited to 0.050% or less. The P content is preferably 0.045% or less, 0.035% or less, or 0.020% or less. The P content may also be 0%, but to make the P content decrease to an extreme degree, the dephosphorization cost increases, therefore from the viewpoint of economy, the lower limit is preferably 0.001%.

[S: 0.0100% or Less]

[0026] S (sulfur) is an element contained as an impurity and forms MnS in steel to cause deterioration of the toughness and hole expandability. Therefore, as a range in which the deterioration of the toughness and hole expandability is not remarkable, the S content is limited to 0.0100% or less. The S content is preferably 0.0050% or less, 0.0040% or less, or 0.0030% or less. The S content may also be 0%, but to make the S content decrease to an extreme degree, the desulfurization cost increases, therefore from the viewpoint of economy, the lower limit is preferably 0.0001%.

[Al: 0.001 to 1.50%]

[0027] Al (aluminum) is added in at least 0.001% for deoxidation of the steel. The Al content may also be 0.005% or more, 0.01% or more, 0.02% or more, 0.05% or more, or 0.10% or more. On the other hand, even if excessively adding Al, the effect becomes saturated and not only is a rise in cost particularly invited, but also the transformation temperature of the steel is made to rise and the load at the time of hot rolling is made to increase. As a result, sometimes the mechanical properties of the steel sheet are made to fall. Therefore, the Al content is given an upper limit of 1.50%. The Al content may also be 1.40% or less, 1.20% or less, or 1.00% or less. Further, Al has the effect of suppressing the formation of iron carbides to thereby make the retained austenite increase. If desiring to obtain this effect, Al has to be added in 0.30% or more. The Al content may also be 0.50% or more or 0.70% or more.

[N: 0.0100% or Less]

[0028] N (nitrogen) is an element contained as an impurity and forms coarse nitrides in the steel to cause deterioration of the bendability and hole expandability if the content is large. Therefore, the N content is limited to 0.0100% or less. The N content is preferably 0.0080% or less, 0.0060% or less, or 0.0050% or less. The N content may also be 0%, but to make the N content decrease to an extreme degree, the denitridation cost increases, therefore from the viewpoint of economy, the lower limit is preferably 0.0001%.

[O: 0.0100% or Less]

[0029] O (oxygen) is an element contained as an impurity and forms coarse oxides in the steel to cause deterioration of the bendability and hole expandability if the content is large. Therefore, the O content is limited to 0.0100% or less. The O content is preferably 0.0080% or less, 0.0060% or less, or 0.0050% or less. The O content may also be 0%, but from the viewpoint of production costs, the lower limit is preferably 0.0001%.

[0030] The basic chemical composition of the base steel sheet according to an embodiment of the present invention and the slab used for its production is as explained above. Furthermore, the base steel sheet and slab may contain the following optional elements in accordance with need. The lower limit of content in the case of not including any optional elements is 0%.

[Cr: 0 to 1.00%, Mo: 0 to 1.00%, Cu: 0 to 1.00%, Ni: 0 to 1.00%, Co: 0 to 1.00%, W: 0 to 1.00%, Sn: 0 to 1.00%, Sb: 0 to 0.50%, Nb: 0 to 0.200%, Ti: 0 to 0.200%, V: 0 to 1.00% and B: 0 to 0.0050%]

[0031] Cr (chromium), Mo (molybdenum), Cu (copper), Ni (nickel), Co (cobalt), W (tungsten), Sn (tin), Sb (antimony), Nb (niobium), Ti (titanium), V (vanadium), and B (boron) are all elements effective for raising the strength of steel sheet. For this reason, one or more of these elements may be added according to need. However, if excessively adding these elements, the effects become saturated and a rise in costs is invited. Therefore, the contents are Cr: 0 to 1.00%, Mo: 0 to 1.00%, Cu: 0 to 1.00%, Ni: 0 to 1.00%, Co: 0 to 1.00%, W: 0 to 1.00%, Sn: 0 to 1.00%, Sb: 0 to 0.50%, Nb: 0 to 0.200%, Ti: 0 to 0.200%, V: 0 to 1.00%, and B: 0 to 0.0050%. The elements may also be 0.001% or more, 0.005% or more, or 0.010% or more. In particular, the B content may also be 0.0001% or more or 0.0002% or more. Similarly, the B content may also be 0.0030% or less, 0.0010% or less, less than 0.0005%, 0.0004% or less, or 0.0003% or less.

[Ca: 0 to 0.0100%, Mg: 0 to 0.0100%, Ce: 0 to 0.0150%, Zr: 0 to 0.0100%, La: 0 to 0.0150%, Hf: 0 to 0.0100%, Bi: 0 to 0.0100% and REM Other Than Ce and La: 0 to 0.0100%]

[0032] Ca (calcium), Mg (magnesium), Ce (cerium), Zr (zirconium), La (lanthanum), Hf (hafnium), and REM (rare earth metal) other than Ce and La are elements contributing to fine dispersion of steel inclusions. Bi (bismuth) is an element lightening the microsegregation of Mn, Si, and other substitution type alloy elements in steel. These contribute to improvement of the workability of steel sheet, therefore one or more of these elements may be added according to need. However, excessive addition triggers deteriorate of the ductility. Therefore, the contents have 0.0150% or 0.0100%

as upper limits. Further, the elements may be 0.0001% or more, 0.0005% or more, or 0.0010% or more.

[0033] In the base steel sheet according to an embodiment of the present invention, the balance besides the above-mentioned elements is comprised of Fe and impurities. "Impurities" are constituents, etc., entering due to various factors in the production process, first and foremost raw materials such as ore and scrap, when industrially producing the base steel sheet.

"Steel Microstructure Inside Base Steel Sheet"

[0034] Next, the reasons for limitation of the internal structure of the base steel sheet according to an embodiment of the present invention will be explained.

[Ferrite: 0 to 50%]

[0035] Ferrite is excellent in ductility, but is a soft structure and is preferably included in accordance with need. The content in this case may be, by vol%, 1% or more, 5% or more, or 10% or more. On the other hand, if excessively containing ferrite, securing the desired steel sheet strength becomes difficult. Therefore, the content is, by vol%, 50% or less and may also be 45% or less, 40% or less, or 35% or less.

[Tempered Martensite: 1% or More]

[0036] Tempered martensite is a high strength and tough structure and a metallographic structure essential in an embodiment of the present invention. To balance strength and elongation at a high level, the tempered martensite content is, by vol%, 1% or more. The tempered martensite content is preferably 5% or more and may be 10% or more or 20% or more. The upper limit is not particularly prescribed, but for example the tempered martensite content may be, by vol%, 90% or less, 80% or less, 70% or less, or 50% or less.

[Retained Austenite: 5% or More]

[0037] Retained austenite improves the ductility of steel sheet by the TRIP effect of transformation to martensite by work induced transformation during deformation of the steel sheet. For this reason, the retained austenite content is, by vol%, 5% or more and may be 8% or more, 9% or more, 10% or more, or 11% or more. Retained austenite rises in elongation the greater the amount, therefore there is no need to prescribe an upper limit value. However, to obtain a large amount of retained austenite, a need arises to include a large amount of C or other alloy elements. In the present invention, an upper limit is set for the C content, therefore it is de facto difficult to obtain 30% or more of retained austenite. Therefore, the retained austenite content may be, by vol%, 30% or less, 25% or less, or 20% or less.

[Fresh Martensite: 0 to 15%]

[0038] In an embodiment of the present invention, "fresh martensite" means martensite which is not tempered, i.e., martensite not containing carbides. This fresh martensite is a brittle structure, therefore becomes starting points of fracture at the time of plastic deformation and causes deterioration of the local ductility of steel sheet. Therefore, the content is, by vol%, 0 to 15%. The fresh martensite content is preferably, by vol%, 0 to 10% or 0 to 5%. The fresh martensite content may also be, by vol%, 1% or more or 2% or more.

[Total Pearlite and Cementite: 0 to 5%]

[0039] Pearlite contains hard and coarse cementite and becomes starting points of fracture at the time of plastic deformation, therefore causes deterioration of the local ductility of steel sheet. Therefore, the content, together with cementite, is, by vol%, 0 to 5% and may be 0 to 3% or 0 to 2%.

[Bainite: Balance]

[0040] The balance of the metallographic structure of the base steel sheet according to an embodiment of the present invention is comprised of bainite. The bainite of the remaining structure may be any of upper bainite having carbides between laths, lower bainite having carbides inside the laths, bainitic ferrite not having carbides, or granular bainite in which the lath boundaries of the bainite have recovered and become unclear or may be mixed structures of the same. The bainite content of the balance may be 0%. For example, the bainite content of the balance may be, by vol%, 1% or more, 5% or more, or 10% or more. The upper limit is not particularly prescribed, but for example the bainite content of the balance may be, by vol%, 70% or less, 60% or less, 57% or less, 55% or less, 50% or less, or 40% or less.

[0041] The percentages of the steel structures are evaluated by secondary electron images obtained using FE-SEM and the X-ray diffraction. First, a sample is taken having a cross-section of thickness parallel to the rolling direction of the steel sheet and at the center position in the width direction as the examined surface. The examined surface is machine polished to finish it to a mirror surface, then is etched using a Nital solution. Next, in one or more examined fields in a range of 1/8 thickness to 3/8 thickness centered on 1/4 thickness from the surface of the base steel sheet at the examined surface, a secondary electron image is captured for a total area of 2.0×10^{-9} m^2 or more. Using the obtained secondary electron image, the area ratios of the ferrite, retained austenite, bainite, tempered martensite, fresh martensite, and pearlite are respectively measured. These are deemed the volume percentages. A region having lower structures inside the grains and precipitating with cementite having several variants is judged tempered martensite. The region where cementite precipitates in a lamellar form is judged to be pearlite (or total of pearlite and cementite). A region with a small luminance and no lower structures recognized are judged to be ferrite. A region with a large luminance and with lower structures not appearing by etching are judged to be fresh martensite and retained austenite. Regions not corresponding to any of the above region are judged to be bainite. The volume ratios of these are calculated by the point counting method and deemed the volume ratios of the structures. The volume ratio of fresh martensite can be found by subtracting the volume ratio of retained austenite found by the X-ray diffraction method.

[0042] The volume ratio of the retained austenite is measured by the X-ray diffraction method. That is, the material of the base steel sheet is removed by machine polishing and chemical polishing down to a depth 1/4 position from the sheet surface in the thickness direction. Further, the polished sample was analyzed using MoKα1 rays as the characteristic X-rays. The structural percentage of retained austenite is calculated from the integrated intensity ratios of the diffraction peaks of the bcc phase (200) and (211) and fee phase (200), (220), and (311). These are made the volume ratios of the retained austenite.

"Hot Dip Galvanized Layer"

[0043] The base steel sheet according to an embodiment of the present invention has a hot dip galvanized layer on at least one surface, preferably on both surfaces. The plating layer may be a hot dip galvanized (GI) layer having any composition known to persons skilled in the art and may contain Al, Mg, Si, Fe, and other added elements besides the Zn. Further, the amount of deposition of the plating layer is not particularly limited and may be a general amount of deposition. The general amount of deposition in the case of use for automobile applications is for example 20 to 100 g/m^2 per surface.

[Number Density of Recessed Parts with Depths of More Than 2 μm at Interface of Base Steel Sheet and Hot Dip Galvanized Layer: 2.0/100 μm or Less Per Interface Length]

[0044] In a hot dip galvanized steel sheet according to an embodiment of the present invention, the number density of recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer is 2.0/100 μm or less per interface length. Recessed parts with depths of more than 2 μm easily accumulate Zn melted by the heat input at the time of spot welding and function as parts where stress concentrates, therefore become starting points of LME cracking. Therefore, if the number density of such recessed parts becomes higher, specifically if that number density becomes more than 2.0/100 μm, the LME cracking sensitivity remarkably deteriorates. For this reason, from the viewpoint of suppression or reduction of LME cracking, it is preferable to reduce the number density of such recessed parts to form a flatter interface shape. Specifically, the number density is more preferably 1.0/100 μm or less. From the viewpoint of suppressing or reducing LME cracking, the smaller the number density of recessed parts with depths of more than 2 μm the more preferable. For this reason, the lower limit of the number density is preferably 0.0/100 μm and may be 0.1/100 μm.

[0045] The number density of recessed parts is measured as follows. Explained in detail referring to FIG. 1, first, a sample is taken having a cross-section of thickness parallel to the rolling direction of the hot dip galvanized steel sheet and at the center position in the width direction as the examined surface. The examined surface is machine polished to finish it to a mirror surface, then a reflected electron image is taken of the plating/steel sheet interface by an imaging power of 500X using FE-SEM (FIG. 1(a)). The obtained reflected electron image is digitalized to clarify the interface of the hot dip galvanized layer and the base steel sheet (FIG. 1(b)). The converted digitalized image is converted to numerical data to obtain the height profile of the interface (FIG. 1(c)). As image analysis software by which such an operation is possible, for example, there are Image J, etc. The center line is found by the least square method from the height profile and a region dissociated to the minus side with a surface height of more than 2 μm from the center line is deemed a "recessed part with a depth of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer". Similar analysis is performed in a total measurement range in the X-direction (rolling) of more than 1 mm. For example if the size in the X-direction (rolling direction) in one field was 200 μm, the above analysis is performed at least five times while changing the field. The numbers of "recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer" obtained at the fields are totaled up and converted to the number density per 100 μm interface length. This is determined as "the number density of recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer". Here, the "interface length" means the length along the height profile of the interface such as shown in FIG. 1(c) and can be measured using image analysis software. As the means for measuring the height profile of steel sheet, the general practice is to use a contact type or laser type roughness meter, but if measuring the interface of plating and a base steel sheet (base iron) like in the present invention, first it is necessary to dissolve and peel off the plating by an acid. However, with this technique, there is a concern that at the time of dissolution by acid, not only the plating, but also the base iron interface will simultaneously be corroded and will change from the original relief shapes, therefore these means are not recommended.

[Maximum Value of Al Concentration of Al Rich Layer Present at Interface of Base Steel Sheet and Hot Dip Galvanized Layer: 2.0 mass% or More]

[0046] The hot dip galvanized steel sheet according to an embodiment of the present invention has an Al rich layer at the interface of the base steel sheet and hot dip galvanized layer. Here, the "Al rich layer" means a region with an Al concentration 10% or more higher than the Al concentration in the hot dip galvanized layer and 10% or more higher than the Al concentration in the base steel sheet. The Al concentration in the hot dip galvanized layer means the Al concentration by a high frequency glow discharge optical emission spectrometer (GDS) at the 1/2 position of the thickness of the hot dip galvanized layer. The 1/2 position of the thickness of the hot dip galvanized layer corresponds to an intermediate position between the interface of the base steel sheet and hot dip galvanized layer identified in measurement by GDS explained later and the surface of the hot dip galvanized steel sheet. Further, the Al concentration in the base steel sheet means the Al concentration corresponding to the average value of the Al emission intensity by GDS at 100 to 150 μm depth from the surface of the hot dip galvanized steel sheet. It is believed that by the presence of the Al rich layer at the interface of the base steel sheet and hot dip galvanized layer, it is possible to suppress the invasion of molten Zn in the base steel sheet. In relation to this, it becomes possible to improve the LME cracking sensitivity. From the viewpoint of reliable improvement of the LME cracking sensitivity, the maximum value of Al concentration of the Al rich layer is 2.0 mass% or more, preferably 2.5 mass% or more. The effect of improvement of the LME cracking sensitivity becomes greater the higher the Al concentration of the Al rich layer. For this reason, the upper limit is not particularly prescribed, but for example the maximum value of the Al concentration of the Al rich layer may be 8.0 mass% or less, 6.0 mass% or less, 5.0 mass% or less, 4.5 mass% or less, or 4.1 mass% or less.

[0047] The maximum value of the Al concentration of the Al rich layer is measured by a high frequency glow discharge optical emission spectrometer (GDS). Specifically, the method is used of rendering the surface of the hot dip galvanized steel sheet an Ar atmosphere, applying voltage to cause the generation of glow discharge, and in that state sputtering the steel sheet surface while analyzing it in the depth direction. Further, from the emission spectrum wavelengths unique to the elements generated by excitation of atoms in the glow plasma, the elements included in the material (hot dip galvanized steel sheet) are identified and the emission intensities of the identified elements are estimated. Data in the depth direction can also be estimated from the sputter time. Specifically, by finding in advance the relationship between the sputter time and sputter depth using standard samples, the sputter time can be converted to sputter depth. Therefore, the sputter depth converted from the sputter time can be defined as the depth from the surface of the material. Further, in the high frequency GDS analysis of the hot dip galvanized steel sheet in the present embodiment, it is possible to use a commercial analysis apparatus. In the present embodiment, a high frequency glow discharge optical emission spectrometer GD-Profiler2 made by Horiba Ltd. is used. The obtained emission intensity is converted to mass% by creating a calibration line in the following way. The average value of the emission intensity is calculated in a range of depth where the emission intensity is sufficiently stable. For example, it is the average value of the emission intensity at 100 to 150 μm depth from the surface of the hot dip galvanized steel sheet. This average value corresponds to the amount of Al [mass%] of the base steel sheet. Further, if the emission intensity is 0, the mass% is also 0. The calibration curve is created by these two points. The position of the interface of the base steel sheet and hot dip galvanized layer can be judged from the emission intensity of Zn.

[0048] One example of the emission intensity of Zn in the case of measurement by GDS is shown in FIG. 2. The position where the emission intensity of Zn sharply falls corresponds to the interface of the base steel sheet and hot dip galvanized layer. Similarly, one example of the Al concentration (emission intensity) in the case of measurement by GDS is shown in FIG. 3. It will be understood that the peak of Al concentration appears at the position where the emission intensity of Zn sharply falls in FIG. 2. The Al concentration calculated from the emission intensity of such a peak appearing at the point where the emission intensity of Zn sharply falls or its vicinity in the case of measurement by GDS (Almax in FIG. 3) is determined as "the maximum value of the Al concentration of the Al rich layer present at the interface of the base steel sheet and hot dip galvanized layer."

[Si_s /Si_b at Base Steel Sheet Right Under Interface of Base Steel Sheet and Hot Dip Galvanized Layer: 0.90 or Less]

[0049] The hot dip galvanized steel sheet according to an embodiment of the present invention has a poor region of Si in the base steel sheet right under the interface of the base steel sheet and hot dip galvanized layer. Here, "right under the interface" means the region up to 10 μm from the interface of the base steel sheet and hot dip galvanized layer in the depth direction. More specifically, it means the region up to 10 μm from the interface of the base steel sheet and hot dip galvanized layer identified by measurement by GDS in the depth direction. Si is an element causing deterioration of the LME cracking sensitivity, therefore by the presence of such an Si poor region in the base steel sheet right under the plating interface contacting the molten Zn, it becomes possible to improve the LME cracking sensitivity. From the viewpoint of reliably improving the LME cracking sensitivity, Si_s /Si_b (where, Si_s is the local minimum value of Si emission intensity at base steel sheet right under interface of base steel sheet and hot dip galvanized layer and Si_b is the average value of Si emission intensity at the base steel sheet) is 0.90 or less, preferably 0.85 or less. The effect of improvement of the LME cracking sensitivity becomes larger the lower the Si_s /Si_b. For this reason, the lower limit is not particularly prescribed, but, for example, Si_s/Si_b may be 0.10 or more, 0.30 or more, 0.50 or more, 0.60 or more, or 0.65 or more. Si_s and Si_b are measured by a high frequency glow discharge optical emission spectrometer (GDS) in the same way as the case of the maximum value of Al concentration of the Al rich layer. Details of the measurement condition are as described in relation to the maximum value of Al concentration of the Al rich layer. The average value need only be calculated in a range of depth where the Si_b emission intensity is sufficiently stable. For example, may be the average value of the emission intensity at a range of 100 to 150 μm depth from the surface of the hot dip galvanized steel sheet. FIG. 4 shows an example of measurement. Referring to FIG. 4, it will be understood that the local minimum value of Si (Si_s) in the base steel sheet right under the interface of the base steel sheet and hot dip galvanized layer appears.

"Mechanical Properties"

[0050] According to the hot dip galvanized steel sheet according to an embodiment of the present invention, excellent mechanical properties, for example, high strength, specifically a 980 MPa or more tensile strength (TS), can be achieved. The tensile strength is preferably 1080 MPa or more, more preferably 1180 MPa or more. The upper limit is not particularly prescribed, but for example the tensile strength may be 2000 MPa or less, 1800 MPa or less, 1600 MPa or less, or 1500 MPa or less. According to the hot dip galvanized steel sheet according to an embodiment of the present invention, similarly, a high ductility can be achieved. More specifically an 8.0% or more, preferably 10.0% or more, more preferably 12.0% or more or 15.0% or more total elongation (El) can be achieved. The upper limit is not particularly prescribed, but for example the total elongation may be 40.0% or less or 35.0% or less. The tensile strength and total elongation are measured by taking a JIS No. 5 tensile test piece from a direction perpendicular to the rolling direction of the steel sheet and conducting a tensile test based on JIS Z2241: 2011. Further, according to the hot dip galvanized steel sheet according to an embodiment of the present invention, a high hole expandability can be achieved. More specifically a 18% or more, preferably 20% or more, more preferably 25% or more hole expansion ratio (λ) can be achieved. The upper limit is not particularly prescribed, but for example the hole expansion ratio may be 80% or less or 70% or less. The hole expansion ratio is measured by conducting a test by the "JFS T 1001 Hole Expansion Test Method" of the Japan Iron and Steel Federation standard. According to the hot dip galvanized steel sheet according to an embodiment of the present invention, the balance of the tensile strength (TS), total elongation (El), and hole expansion ratio (λ) can be improved at a high level, therefore it is possible to achieve a press-formability preferable for use as a member for automotive use.

[Sheet Thickness]

[0051] The hot dip galvanized steel sheet according to an embodiment of the present invention has a thickness of, for example, 0.6 to 4.0 mm. While not particularly limited, the sheet thickness may be 0.8 mm or more, 1.0 mm or more, or 1.2 mm or more. Similarly, the sheet thickness may be 3.0 mm or less, 2.5 mm or less, or 2.0 mm or less.

"Production Method"

[0052] Next, the method for producing the hot dip galvanized steel sheet will be explained. The following explanation is intended to illustrate the characteristic method for producing the hot dip galvanized steel sheet according to an embodiment of the present invention and is not intended to limit the hot dip galvanized steel sheet by the production method such as explained below.

"(A) Hot Rolling Step"

[0053] First, in the hot rolling step, a slab having the same chemical composition as the chemical composition explained relating to the base steel sheet is heated before hot rolling, then is subjected to rough rolling and finish rolling. The heating temperature of the slab is not particularly limited, but generally preferably is 1150°C or more so as to sufficiently dissolve borides, carbides, etc. The steel slab used is preferably cast by the continuous casting method from the viewpoint of manufacturability, but may also be produced by the ingot casting method or thin slab casting method.

[Rough Rolling]

[0054] The heated slab may also be rough rolled before finish rolling. The rough rolling conditions are not particularly limited, but the rough rolling is preferably performed so that the end temperature becomes 1050°C or more and the total rolling reduction becomes 60% or more. If the total rolling reduction is less than 60%, the recrystallization during hot rolling becomes insufficient, therefore this sometimes leads to uneven quality of the hot rolled steel sheet structure. The total rolling reduction, for example, may be 90% or less.

[Finish Rolling]

[0055] After the optional rough rolling, the steel sheet is finish rolled. The conditions are not particularly limited, but the step is preferably performed in a range satisfying the conditions of a finish rolling entry side temperature of 950 to 1 100°C, a finish rolling exit side temperature of 850 to 1000°C, and a total rolling reduction of 80 to 95%. If the finish rolling entry side temperature falls below 950°C, the finish rolling exit side temperature falls below 850°C, or the total rolling reduction rises above 95%, the hot rolled steel sheet is forms texture, therefore sometimes the anisotropy at the final product sheet becomes remarkable. On the other hand, if the finish rolling entry side temperature rises above 1 100°C, the finish rolling exit side temperature rises above 1000°C, or the total rolling reduction falls below 80%, sometimes the grain size of the hot rolled steel sheet becomes coarser and coarsening of the structure of the final product sheet is triggered.

[Coiling Temperature]

[0056] The hot rolled steel sheet after finish rolling is, for example, cooled to 700°C or less, then taken up in a coil. The coiling temperature is preferably 450 to 680°C. If the coiling temperature falls below 450°C, sometimes the strength of the hot rolled sheet becomes excessive and the cold rollability is impaired. On the other hand, if the coiling temperature rises above 680°C, Mn and other alloy elements concentrate at the cementite, therefore in the final annealing step, sometimes cementite is slow to dissolve and a drop in strength is triggered. The coiling temperature may be 500°C or more and/or may be 650°C or less or 600°C or less.

[Cooling of Hot Rolled Coil After Coiling]

[0057] The hot rolled coil after coiling (hot rolled steel sheet) is cooled so as to satisfy the following formula (1).
[Mathematical 5]

$$0.05 < \sqrt{2 \cdot \sum_{t=0}^{tf} \left(\frac{Do \cdot No}{N_x} \cdot \Delta t \right)} < 1.50 \quad \cdots \quad (1)$$

where,
[Mathematical 6]

$$D_o = 2.9 \cdot 10^{-7} \cdot exp\left(- \frac{90{,}000}{8.314 \cdot T(t)} \right) \quad \cdots \quad (2)$$

[Mathematical 7]

$$N_o = 0.381 \cdot exp\left(- \frac{104{,}000}{8.314 \cdot T(t)} \right) \quad \cdots \quad (3)$$

T(t): steel sheet temperature (K) after elapse of "t" seconds from coiling
tf: time (s) until steel sheet temperature reaches 673K
Nx: total of atomic percents (-) of Si, Mn, and Al in steel

[0058] Formula (1) shows that the greater the Σ value, the more an internal oxidation reaction proceeds at the steel sheet surface. The Σ in formula (1) is calculated by quadrature by parts. Δt is a finite value and corresponds to the measurement pitch of temperature T(t). For example, it is 100 seconds. Do is the diffusion coefficient of oxygen atoms at the temperature T(t), No is amount of oxygen atoms dissolved in the steel at the temperature T(t), and Nx is the total amount of the main elements to be internally oxidized in the steel. Nx can be calculated by converting the mass percentages of the elements (Si, Mn, Al) to atomic percentages and adding them up. If converting this to a formula, the result becomes the formula (5). [Mathematical 8]

$$N_x = \frac{[Si]/_{M_{Si}} + [Mn]/_{M_{Mn}} + [Al]/_{M_{Al}}}{[Fe]/_{M_{Fe}} + [C]/_{M_C} + [Si]/_{M_{Si}} + [Mn]/_{M_{Mn}} + [P]/_{M_{Al}} + [S]/_{M_{Al}} + [Al]/_{M_{Al}} + [N]/_{M_N} \cdots} \cdots (5)$$

where, [X] is the mass percentage of the element X and Mx is the atomic percentage of the element X. The denominator of the formula (5) is the total of all elements added to the steel in question.

[0059] That is, formula (1) means that the greater the diffusion coefficient of oxygen atoms or the greater the amount of dissolved oxygen, the easier it is for the internal oxidation reaction to proceed and the greater the amount of elements to be internally oxidized, the harder it is for it to proceed. If the internal oxidation reaction proceeds, the Si dissolved in the steel is consumed by the formation of internal oxides, therefore an Si poor layer is formed right under the internal oxidation layer. Here, Si, in particular the Si dissolved in the steel, is an element causing the deterioration of the LME cracking sensitivity. On the other hand, this Si poor layer can be made to remain in up to the final product by limiting the pickling conditions as explained later. Due to this, it is possible to decrease the amount of Si dissolved in the base steel sheet right under the interface with the molten Zn. For this reason, the LME resistance can be remarkably improved. On the other hand, if excessively proceeding with the internal oxidation reaction, the relief shapes of the steel sheet become larger after pickling. These relief shapes are flattened to a certain extent by the cold rolling, but the effect remains up to the final product. As a result, the number density of recessed parts with depths of more than 2 μm at the steel sheet/plating interface of the final product increases and the LME resistance deteriorates. Due to such a situation, the value of formula (1) is limited to more than 0.05 to less than 1.50. Preferably, it is 0.10 to 1.00, more preferably 0.20 to 0.70.

[0060] "(B) Pickling Step"

[0061] The hot rolled steel sheet obtained in the hot rolling step is pickled by running it through a temperature 70 to 90°C aqueous solution containing 1.0 to 5.0 mol/L of HCl, less than 3.0 mol/L of Fe^{2+}, and less than 0.10 mol/L of Fe^{3+} by an average speed of 10 m/min or more for 30 seconds or more. At this time, to efficiently remove the internal oxidation layer containing the Si oxides, etc., the hot rolled steel sheet before pickling is deformed by bending and unbending at least once by a tension leveler, etc. If the HCl concentration in the pickling solution falls below 1.0 mol/L, the Fe^{2+} concentration becomes 3.0 mol/L or more, the temperature of the aqueous solution falls below 70°C, the average speed of the hot rolled steel sheet falls below 10 m/min, or the pickling time falls below 30 seconds, the pickling does not sufficiently proceed and the internal oxidation layer is unevenly removed. As a result, the number density of recessed parts with depths of more than 2 μm at the steel sheet/plating interface of the final product increases. On the other hand, if the HCl concentration rises above 5.0 mol/L or the temperature rises above 90°C, pickling excessively proceeds, even the Si poor region which had been formed at the hot rolled steel sheet is removed, and the Si poor region right under the interface of the base steel sheet and hot dip galvanized layer of the final product is insufficiently formed. Further, it is known that the Fe^{3+} in the pickling solution suppresses the effect of the inhibitor and thereby promotes the dissolution of the base steel sheet. If the Fe^{3+} content is 0.10 mol/L or more, the effect becomes remarkable. As a result, again, the Si poor region right under the interface of the base steel sheet and hot dip galvanized layer of the final product is insufficiently formed. Due to the above reason, the pickling conditions are limited as explained above.

"(C) Cold Rolling Step"

[0062] The hot rolled steel sheet after pickling is then cold rolled. The rolling reduction of the cold rolling is 30% or more so as to promote recrystallization and/or flatten relief shapes of steel sheet after pickling. If the rolling reduction is less than 30%, the relief shapes at the steel sheet surface cannot be sufficiently flattened and the number density of recessed parts with depths of more than 2 μm at the steel sheet/plating interface of the final product increases. The rolling reduction may also be 40% or more. On the other hand, excessive rolling reduction causes excessive rolling load and invites an increase in load of the cold rolling mill, therefore the upper limit is 75% or 70%.

"(D) Heat Treatment and Plating Step"

[(D1) Average heating speed from 600°C to an Ac1+30°C to 950°C maximum heating temperature of 0.2 to 20°C/s]

[0063] Next, the obtained cold rolled steel sheet is subjected to predetermined heat treatment and plating at the heat treatment and plating step. Specifically, first, the cold rolled steel sheet is heated so that the average heating speed from 600°C to an Ac1+30°C to 950°C maximum heating temperature becomes 0.2 to 20°C/s and an atmosphere around the cold rolled steel sheet satisfies the following formula (4):
[Mathematical 9]

$$-1.0 < \log\left(\frac{pH_2O}{pH_2}\right) < -0.1 \quad \cdot\cdot\cdot \quad (4)$$

pH_2 O: steam partial pressure
pH_2 : hydrogen partial pressure

[0064] An internal oxidation reaction proceeds not only at the hot rolling step, but also the heat treatment step after the cold rolling, whereby formation of the Si poor part is further promoted. The log(pH_2 O/pH_2) of formula (4) is also called the "oxygen potential". The larger this value, the more internal oxidation of the Si, Mn, Al, and other easily oxidizable elements present at the surface layer part in the steel proceeds and the Si poor region grows more. To obtain this effect, at the very least, this value has to be more than -1.0. On the other hand, if the value is more than -0.1, not only Si, Mn, Al, etc., but even Fe proceed to oxidize, whereby nonplating and other problems arise. The more preferable range is -0.9 to -0.2, more preferably -0.8 to -0.3. The maximum heating temperature from 600°C to the Ac1+30°C to 950°C is limited to 0.2 to 20°C/s. If more than 20°C/s, the internal oxidation reaction does not sufficiently proceed. On the other hand, if less than 0.2°C/s, coarsening of the structure and the decarburization reaction excessively proceed and thereby the strength falls. The preferable average heating speed is 0.5 to 10°C/s, more preferably 1 to 7°C/s. Acl (°C) is calculated by the following formula: At the symbols of the elements in the following formula, the mass% of the elements in the base steel sheet are entered. For the elements not contained, 0 mass% is entered.

$$Ac1(°C)=723-10.7\times Mn-16.9\times Ni+29.1\times Si+16.9\times Cr$$

[(D2) Holding at maximum heating temperature of Ac1+30°C to 950°C for 1 to 1000 seconds]

[0065] To make the austenite formation sufficiently proceed and obtain the desired microstructure by the subsequent cooling treatment, the cold rolled steel sheet is heated to at least the Ac1+30°C or more and soaking is performed at that temperature (maximum heating temperature). If austenite is not sufficiently formed, sometimes ferrite is formed in a large amount at the final structure. However, if excessively raising the heating temperature, not only is deterioration of the toughness due to coarsening of the austenite grain size, but also damage to the annealing facilities is caused. For this reason, the upper limit is 950°C, preferably 900°C. If the soaking time is short, the formation of austenite does not sufficiently proceed, therefore it is at least 1 second or more. The soaking time is preferably 30 seconds or more or 60 seconds or more. On the other hand, if the soaking time is too long, the productivity is obstructed, therefore the upper limit is 1000 seconds, preferably 600 seconds. During soaking, the cold rolled steel sheet does not necessarily have to be held at a constant temperature and may fluctuate within a range satisfying the above conditions.

[(D3) Time after dipping in plating bath until gas wiping is 0.1 to 5 seconds and steel sheet temperature after gas wiping is 440°C or less]

[0066] The cold rolled steel sheet after the heating and holding is cooled and dipped in a hot dip galvanization bath. At this time, the steel sheet is preferably cooled so that the average cooling speed in the 550 to 700°C temperature range becomes 10 to 100°C/s. Regarding the steel sheet temperature at the time of dipping in the hot dip galvanization bath, if the difference between the steel sheet temperature and the plating bath temperature is too great, sometimes the plating bath temperature changes and the operation is obstructed. For this reason, the steel sheet temperature is preferably the plating bath temperature-20°C to the plating bath temperature+20°C. The hot dip galvanization may be performed in accordance with the usual method. For example, the plating bath temperature may be 440 to 480°C, and the dipping time may be 5 seconds or less. To form an Al rich layer at the steel sheet/plating interface, the plating bath preferably contains Al in 0.1 to 0.5 mass%. In addition, as impurities, Fe, Si, Mg, Mn, Cr, Ti, Pb, etc., may be contained. The basis weight of the plating is controlled by the gas wiping. The basis weight may be suitably changed in accordance with the corrosion resistance demanded, but, or example, 20 to 100 g/m^2 per surface is preferable. The time until gas wiping after dipping in the plating bath is limited to 0.1 to 5 seconds. If the time rises above 5 seconds or the steel sheet temperature after gas wiping rises above 440°C, the Al rich layer starts to fracture, therefore the maximum value of the Al concentration in the Al rich layer present at the steel sheet/plating interface falls below a predetermined value. The lower limit is not particularly prescribed, but, for example, the steel sheet temperature after gas wiping may be 300°C or more. On the other hand, the lower limit of the time until gas wiping is determined by the hardware configuration, but on a usual hot dip galvanization line, making it lower than 0.1 second is difficult.

[(D4) Cooling steel sheet to Ms to Ms-200°C in range, then reheating it to 300 to 420°C temperature region and holding it at that temperature region for 100 to 600 seconds]

[0067] To cause part of the nontransformed austenite transform to martensite, the steel sheet is cooled to the martensite transformation start temperature (Ms) to Ms-200°C in range. The martensite formed here is tempered by later reheating and holding treatment and becomes tempered martensite. If the cooling step temperature rises above Ms, the tempered martensite is not formed, therefore the desired metallographic structure is not obtained. On the other hand, if the cooling stop temperature falls below Ms-200°C, the nontransformed austenite is excessively decreased, therefore the desired retained austenite content is not obtained. The preferable range of the cooling stop temperature is Ms-20 to Ms-150°C, more preferably Ms-40 to Ms-100°C. Martensite transformation occurs after ferrite transformation and/or bainite transformation. Along with the above transformation, C is distributed in the austenite. For this reason, this does not match with the Ms when heating to the austenite single phase and rapidly cooling. The Ms in an embodiment of the present invention is found by measuring the thermal expansion temperature. For example, Ms can be found by using a Formaster tester or other apparatus able to measure the amount of thermal expansion during continuous heat treatment to reproduce the heat cycle from the start of heat treatment (corresponding to room temperature) to cooling to the Ms or less and measure the amount of thermal expansion during that time. In the temperature-thermal expansion curve at the time of simulating the heat cycle by a thermal expansion measurement apparatus, the steel sheet thermally contracts linearly during cooling, but deviates from a linear relationship at a certain temperature. The temperature at this time is Ms in an embodiment of the present invention.

[0068] After cooling to Ms to Ms-200°C in range, the steel sheet is reheated and held at 300°C to 420°C in range. In this treatment, to obtain the desired retained austenite content, carbon is made to concentrate in the austenite and the austenite is made to stabilize (austempering). At the same time, the martensite formed by the cooling is tempered. If the reheating temperature is less than 300°C or the holding time is less than 100 seconds, the carbon is insufficiently concentrated at the austenite. In the process of cooling to room temperature after that, the ratio of the austenite remaining in the nontransformed austenite until room temperature and becoming retained austenite is decreased and the ratio of formation of fresh martensite increases. As a result, the content of the retained austenite falls below, by vol%, the lower limit of 5% and/or the content of the fresh martensite rises above, by vol%, 15%. On the other hand, if the reheating temperature rises above 420°C or the holding time rises above 600 seconds, the austenite breaks down into cementite, therefore the desired retained austenite content is not obtained. The order of (D3) and (D4) is not an issue. For example, after dipping in the plating bath, the steel sheet may be cooled to Ms to Ms-200°C in range and dipped in the plating bath after finishing the step of (D4).

[0069] Finally, the steel sheet is cooled down to room temperature to obtain the final product. To flatten and correct the steel sheet and adjust the surface roughness, temper rolling may be performed. In this case, to avoid deterioration of the ductility, the elongation rate is preferably 2% or less.

EXAMPLES

[0070] Next, examples of the present invention will be explained. The conditions of the examples are illustrations of the conditions employed for confirming the workability and effect of the present invention. The present invention is not limited to these illustrations of conditions. The present invention can employ various conditions so long as not deviating from the gist of the present invention and achieving the object of the present invention.

[0071] Steels having the chemical compositions shown in Table 1 were cast to prepare slabs. The balances other than the constituents shown in Table 1 were comprised of Fe and impurities. These slabs were hot rolled, including rough rolling and finish rolling, under the conditions shown in Table 2 to produce hot rolled steel sheets. After that, the steel sheets were coiled and cooled under the conditions shown in Table 2. Next, a tension leveler was used to deform the steel sheets by at least one bending and unbending operation, then the hot rolled steel sheets were pickled under the conditions shown in Table 2 to remove the internal oxidation layers and then were cold rolled. The sheet thicknesses after the cold rolling were 1.6 mm in each case. The obtained cold rolled steel sheets were further heat treated and hot dip galvanized (GI) under the conditions shown in Table 2.

[0072] JIS No. 5 tensile test pieces were taken from a direction perpendicular to the rolling direction of the hot dip galvanized steel sheets obtained in the above way and tensile tests based on JIS Z2241: 2011 to measure the tensile strength (TS) and total elongation (El). Further, the "JFS T 1001 Hole Expansion Test Method" of the Japan Iron and Steel Federation standard was used to measure the hole expansion ratio (λ). Samples with a TS of 980 MPa or more and a $TS\times El\times\lambda^{0.5}/1000$ of 90 or more were excellent in mechanical properties and judged to have press-formability preferable for use as members for automotive use.

[0073] Further, to evaluate the liquid metal embrittlement (LME) fracturing ability of the spot welds, 150 mm width×50 mm length test pieces were obtained and pairs were subjected to spot welding tests. The sheets were made pairs of the same steel sheets shown in Table 3 which were welded in the state with weld angles of 3°. For the test apparatus, a servo motor-driven type stationary spot welding test apparatus was used. The power source was made a single-phase AC 50Hz, weld pressure 400 kgf, weld time 20 cycles, and hold time 5 cycles. The values of the weld currents were made values of currents giving diameters of the molten nuggets of 4.0 times, 5.0 times, and 5.5 times of $\sqrt{t}$ (t: sheet thickness/mm). For the electrodes, electrodes made of chrome copper with tip diameters of ϕ6 mm and tip bending radii R of 40 mm were used. The welded samples were examined at cross-sections of the nugget parts. Samples with 0.2 mm or more cracks observed at any of the current values were judged as "P" (poor), samples with 0.1 mm or more and less than 0.2 mm cracks observed at any of the current values were judged as "G" (good), and samples with less than 0.1 mm cracks observed at any of the current values were evaluated as "VG" (very good). The results are shown in Table 3.

[Table 1]

[0074]

Table 1

Steel type	Chemical composition (mass%, bal. Fe and impurities)																					Ac1
	C	Si	Mn	P	S	Al	N	O	Cr	Mo	Cu	Ni	Co	W	Sn	Sb	Nb	Ti	V	B	Others	
A	0.23	0.80	2.52	0.013	0.0004	0.46	0.0027	0.0004														719
B	0.15	1.14	2.23	0.020	0.0027	0.11	0.0019	0.0011										0.025		0.0014		732
C	0.26	1.45	1.45	0.016	0.0027	0.02	0.0023	0.0009	0.29	0.07								0.013		0.0023		755
D	0.21	0.37	2.56	0.003	0.0006	1.35	0.0015	0.0010			0.30	0.15										704
E	0.22	0.63	2.30	0.011	0.0023	0.74	0.0034	0.0010										0.020		0.0018		717
F	0.19	1.02	2.01	0.018	0.0010	0.53	0.0025	0.0012	0.15						0.36		0.018	0.016				734
G	0.30	0.66	2.48	0.020	0.0023	0.05	0.0020	0.0006					0.22								La:0.0049	716
H	0.22	1.61	2.14	0.005	0.0021	0.03	0.0018	0.0005													Ca:0.0025	747
I	0.18	0.87	3.45	0.013	0.0013	0.36	0.0027	0.0007														711
J	0.21	0.79	2.69	0.016	0.0019	1.10	0.0027	0.0007										0.021		0.0011	Mg:0.0037	717
K	0.22	0.94	2.64	0.006	0.0030	0.06	0.0042	0.0009								0.12		0.052		0.0037		722
L	0.24	1.17	2.55	0.018	0.0013	0.35	0.0020	0.0012									0.030		0.34		REM:0.0054	730
M	0.21	1.78	2.41	0.018	0.0029	0.01	0.0019	0.0008										0.018		0.0017	Ce:0.0060	749
N	0.20	0.81	2.57	0.003	0.0024	0.80	0.0042	0.0005		0.15								0.024		0.0025		719
O	0.23	0.99	1.96	0.015	0.0012	0.48	0.0022	0.0005	0.81	0.10				0.31								745
P	0.16	1.03	2.97	0.015	0.0013	0.61	0.0041	0.0011												0.0020	Bi:0.0043	721
Q	0.28	1.66	3.24	0.017	0.0028	0.07	0.0022	0.0005			0.42							0.023		0.0015	Zr:0.0018,Hf:0.0081	737
R	0.29	2.37	2.32	0.004	0.0025	0.05	0.0037	0.0010	0.78									0.033		0.0022		780
S	0.26	1.04	2.91	0.012	0.0009	0.02	0.0040	0.0012		0.43		0.80					0.015	0.027		0.0013		709
T	0.24	0.33	3.05	0.009	0.0026	0.02	0.0015	0.0004										0.021		0.0017		700
U	0.11	1.30	2.46	0.007	0.0015	0.05	0.0018	0.0004														735
V	0.35	1.06	2.60	0.004	0.0023	0.04	0.0028	0.0012														726
W	0.24	0.20	2.66	0.013	0.0017	0.08	0.0041	0.0003														700
X	0.20	2.69	2.38	0.019	0.0029	0.03	0.0020	0.0010														776
Y	0.28	1.15	1.30	0.010	0.0008	0.10	0.0021	0.0008														743
Z	0.17	0.77	3.68	0.011	0.0016	0.05	0.0023	0.0010														706
AA	0.21	0.56	2.50	0.005	0.0020	1.69	0.0033	0.0009														713

Underlines indicated outside scope of present invention.

[Table 2-1]

[0075]

Table 2-1

No.	Steel type	(A) Hot rolling step								(B) Pickling step					
		Slab heating temp.	Rough rolling		Finish rolling			Coiling temp.	Value of formula (1)	[HCl]	[Fe^{2+}]	[Fe^{3+}]	Pickling bath temp.	Average temp.	Time
			End temp.	Total rolling reduction	Entry temp.	Exit temp.	Total rolling reduction								
		°C	°C	%	°C	°C	%	°C		mol/L	mol/L	mol/L	°C	m/min	sec
1	A	1270	1120	85	1070	970	91	570	0.29	2.4	1.3	0.02	80	70	50
2	A	1250	1090	85	1040	910	91	620	0.25	2.3	1.2	0.03	80	70	50
3	A	1250	1100	85	1050	920	91	550	0.20	2.7	1.0	0.01	80	70	50
4	A	1240	1070	85	980	900	91	580	0.34	2.5	1.9	0.57	80	70	50
5	A	1220	1100	85	1050	930	91	600	0.46	0.6	1.6	0.03	80	70	50
6	A	1260	1090	85	1050	940	91	650	1.80	2.8	1.5	0.03	80	70	50
7	A	1240	1090	85	1060	960	91	560	0.03	2.4	1.1	0.01	80	70	50
8	A	1230	1060	85	1000	890	91	600	0.53	2.5	5.8	0.02	80	70	50
9	A	1270	1140	92	1090	990	85	500	0.07	2.6	1.0	0.02	80	70	50
10	A	1270	1130	85	1060	960	91	550	0.20	7.0	1.5	0.01	80	70	50
11	B	1220	1080	85	1040	960	91	540	0.21	2.6	1.0	0.04	72	55	64
12	C	1220	1100	85	1020	920	91	550	0.22	2.7	1.4	0.01	85	80	44
13	D	1270	1120	85	1050	940	91	530	0.13	2.3	1.5	0.02	80	80	44
14	E	1240	1100	85	1020	890	91	550	0.22	2.5	1.1	0.01	80	70	50
15	E	1220	1130	85	1080	990	87	540	0.19	2.3	1.0	0.02	90	70	50
16	E	1250	1100	85	1060	910	91	600	0.13	2.3	1.2	0.03	80	70	50
17	E	1230	1090	85	1010	890	91	560	0.26	2.5	1.2	0.01	80	70	50
18	E	1240	1100	85	1010	880	91	550	0.18	2.1	1.2	0.01	80	70	50
19	E	1220	1080	85	1030	920	91	580	0.50	2.6	1.3	0.02	80	70	50
20	E	1240	1090	85	1020	930	91	560	0.31	2.8	1.3	0.02	80	70	50
21	E	1270	1150	85	1080	970	91	550	0.30	2.4	1.0	0.02	80	70	50

(continued)

No.	Steel type	(A) Hot rolling step								(B) Pickling step					
		Slab heating temp.	Rough rolling		Finish rolling			Coiling temp.	Value of formula (1)	[HCl]	[Fe^{2+}]	[Fe^{3+}]	Pickling bath temp.	Average temp.	Time
			End temp.	Total rolling reduction	Entry temp.	Exit temp.	Total rolling reduction								
		°C	°C	%	°C	°C	%	°C		mol/L	mol/L	mol/L	°C	m/min	sec
22	E	1220	1070	85	1010	920	91	550	0.33	2.4	1.1	0.01	80	70	50
23	F	1220	1060	85	990	870	91	590	0.41	1.8	2.3	0.06	80	70	50
24	F	1250	1070	85	1000	900	91	570	1.03	2.4	0.9	0.02	80	70	50
25	G	1270	1130	85	1060	970	91	590	0.76	2.0	1.3	0.02	80	70	50
26	H	1230	1090	85	1000	920	91	550	0.19	2.7	0.6	0.03	80	70	50
27	I	1260	1130	85	1070	940	91	600	0.49	3.2	1.5	0.02	80	70	50

Underlines indicated outside scope of present invention.

[Table 2-2]

[0076]

Table 2-2

No.	Steel type	(A) Hot rolling step								(B) Pickling step					
		Slab heating temp.	Rough rolling		Finish rolling			Coiling temp.	Value of formula (1)	[HCl]	$[Fe^{2+}]$	$[Fe^{3+}]$	Pickling bath temp.	Average temp.	Time
			End temp.	Total rolling reduction	Entry temp.	Exit temp.	Total rolling reduction								
		°C	°C	%	°C	°C	%	°C		mol/L	mol/L	mol/L	°C	m/min	sec
28	J	1240	1090	85	1000	900	91	580	0.48	2.2	1.7	0.05	80	70	50
29	K	1250	1120	85	1050	930	91	610	0.77	2.3	1.2	0.02	80	70	50
30	L	1230	1110	85	1040	930	91	590	0.29	2.9	0.9	0.03	80	70	50
31	M	1250	1100	85	1050	950	91	550	0.17	2.5	1.0	0.01	80	70	50
32	N	1230	1090	85	1020	920	91	630	0.75	2.1	1.2	0.02	80	70	50
33	N	1260	1100	85	1050	930	91	600	0.30	2.2	1.0	0.02	80	70	50
34	N	1240	1080	85	1030	890	91	570	0.23	2.2	1.1	0.02	80	70	50
35	N	1210	1070	85	1010	910	91	580	0.15	2.3	1.6	0.03	80	70	50
36	N	1250	1100	90	1000	870	93	610	0.89	2.4	1.1	0.02	80	70	50
37	N	1250	1120	85	1070	950	91	590	0.55	2.8	1.0	0.01	80	70	50
38	N	1240	1120	85	1040	900	91	590	0.61	3.1	1.3	0.02	95	70	50
39	N	1270	1150	85	1070	960	91	580	0.46	2.7	1.2	0.02	60	70	50
40	O	1230	1080	85	1030	940	91	600	0.34	2.3	1.4	0.03	80	70	50
41	P	1260	1100	85	1010	910	91	560	0.20	2.2	0.8	0.01	80	70	50
42	Q	1220	1090	85	1010	890	91	620	0.44	2.6	0.9	0.02	80	70	50
43	R	1270	1100	85	1040	960	91	610	0.40	2.8	1.3	0.04	80	70	50
44	S	1250	1090	85	1020	890	91	600	0.32	2.4	0.8	0.01	80	70	50
45	T	1230	1110	85	1050	950	91	540	0.11	3.6	1.1	0.03	80	70	50
46	U	1250	1120	85	1030	920	91	580	0.43	3.0	1.5	0.01	80	70	50
47	V	1250	1080	85	1000	870	91	560	0.28	1.6	1.2	0.02	80	70	50
48	W	1270	1140	85	1060	950	91	550	0.14	2.5	1.0	0.01	80	70	50

(continued)

No.	Steel type	(A) Hot rolling step								(B) Pickling step					
		Slab heating temp.	Rough rolling		Finish rolling			Coiling temp.	Value of formula (1)	[HCl]	$[Fe^{2+}]$	$[Fe^{3+}]$	Pickling bath temp.	Average temp.	Time
			End temp.	Total rolling reduction	Entry temp.	Exit temp.	Total rolling reduction								
		°C	°C	%	°C	°C	%	°C		mol/L	mol/L	mol/L	°C	m/min	sec
49	X	1220	1100	85	1040	920	91	630	0.90	2.8	1.2	0.02	80	70	50
50	Y	1260	1130	85	1070	980	91	580	0.23	2.7	1.5	0.02	80	70	50
51	Z	1250	1080	85	1010	920	91	600	0.42	2.6	1.3	0.02	80	70	50
52	AA	1230	1070	85	980	860	91	590	0.51	3.0	1.1	0.03	80	70	50
53	A	1260	1090	85	1040	920	91	590	0.32	2.4	1.1	0.02	80	70	28
54	B	1240	1100	85	1040	910	91	560	0.38	2.6	1.3	0.02	80	70	24

Underlines indicated outside scope of present invention.

[Table 2-3]

[0077]

Table 2-3

No.	(C) Cold rolling step	(D) Heat treatment and plating step										
		(D1)			(D2)	(D3)		(D4)				
	Rolling reduction	Average heating speed of 600°C to max. heating temp.	Max. heating temp.	Value of formula (4)	Holding time	Plating bath dipping-gas wiping time	Steel sheet temp. after gas wiping	Cooling temp.	Ms-cooling temp.	Reheating temp.	Holding time	Ms
	%	°C/s	°C		sec	sec	°C	°C	°C	°C	sec	°C
1	53	2.3	820	-0.6	80	3	420	50	153	370	180	203
2	53	2.2	820	-0.6	80	3	420	170	22	360	180	192
3	53	2.7	840	-1.0	20	3	420	120	166	370	180	286
4	53	2.1	810	-0.6	80	3	410	50	138	370	180	188
5	53	3.0	860	-0.6	80	3	420	150	148	360	180	298
6	53	2.8	850	-0.6	80	3	420	50	152	370	180	202
7	53	2.2	830	-0.7	80	3	420	90	135	400	180	225
8	53	2.4	810	-0.6	80	3	420	60	129	360	180	189
9	53	2.5	810	-0.6	80	3	420	100	165	370	180	265
10	53	2.5	820	-0.6	80	3	420	70	125	370	180	195
11	53	4.0	800	-0.8	50	2	430	180	167	340	120	347
12	53	3.1	850	-0.5	80	3	420	60	118	360	180	178
13	53	4.3	900	-0.5	80	3	420	50	113	370	180	163
14	53	2.2	810	-0.6	80	3	420	80	166	350	180	246
15	70	2.5	820	-0.5	80	3	430	80	150	360	180	230
16	53	1.3	700	-0.6	80	3	440	80	-	360	180	-
17	53	2.4	800	-0.6	80	7	410	70	162	350	180	232
18	53	2.2	810	-0.6	80	2	460	100	159	360	180	259
19	53	2.3	830	-1.3	80	3	430	70	163	380	180	233

(continued)

No.	(C) Cold rolling step	(D) Heat treatment and plating step										
	Rolling reduction	(D1)			(D2)	(D3)		(D4)				
		Average heating speed of 600°C to max. heating temp.	Max. heating temp.	Value of formula (4)	Holding time	Plating bath dipping-gas wiping time	Steel sheet temp. after gas wiping	Cooling temp.	Ms-cooling temp.	Reheating temp.	Holding time	Ms
	%	°C/s	°C		sec	sec	°C	°C	°C	°C	sec	°C
20	53	2.3	820	-0.5	80	3	430	80	180	260	180	260
21	53	2.4	820	-0.6	80	3	430	290	-13	390	180	277
22	53	2.1	810	-0.5	80	3	420	100	173	360	75	273
23	53	2.6	830	-0.6	80	3	420	90	165	360	180	255
24	53	2.9	840	-0.6	80	3	430	70	178	370	180	248
25	53	1.7	790	-0.4	80	3	440	40	96	390	180	136
26	53	2.8	830	-0.3	80	3	410	50	168	410	180	218
27	53	3.0	840	-0.7	80	3	400	230	106	360	180	336
Underlines indicated outside scope of present invention.												

[Table 2-4]

[0078]

Table 2-4

No.	(C) Cold rolling step	(D) Heat treatment and plating step										
		(D1)			(D2)	(D3)		(D4)				
	Rolling reduction	Average heating speed of 600°C to max. heating temp.	Max. heating temp.	Value of formula (4)	Holding time	Plating bath dipping-gas wiping time	Steel sheet temp. after gas wiping	Cooling temp.	Ms-cooling temp.	Reheating temp.	Holding time	Ms
	%	°C/s	°C		sec	sec	°C	°C	°C	°C	sec	°C
28	53	5.3	900	-0.5	80	3	420	220	117	400	180	337
29	53	2.2	820	-0.7	80	3	430	240	102	380	180	342
30	53	3.9	880	-0.6	80	2	430	260	90	420	180	350
31	53	3.3	850	-0.7	80	3	420	250	98	350	180	348
32	53	3.0	850	-0.4	80	3	430	220	131	400	180	351
33	53	3.6	860	-0.5	80	2	430	250	87	480	180	337
34	53	3.1	850	-0.5	80	2	430	240	101	390	900	341
35	53	3.1	850	-0.5	80	3	420	50	303	400	180	353
36	22	3.4	860	-0.6	80	3	420	230	126	400	180	356
37	53	2.9	840	0	80	2	430	250	91	400	180	341
38	53	4.6	880	-0.6	80	3	420	250	112	380	180	362
39	53	3.0	850	-0.6	80	3	420	260	88	390	180	348
40	53	3.7	860	-0.7	80	3	430	230	102	370	180	332
41	53	4.3	880	-0.6	80	3	420	200	165	340	180	365
42	53	3.5	870	-0.6	80	3	420	210	99	340	180	309
43	53	5.3	900	-0.6	80	3	420	220	96	350	180	316
44	53	4.2	880	-0.6	80	3	430	230	95	360	180	325
45	53	5.0	850	-0.7	80	3	420	220	124	310	180	344
46	53	3.2	840	-0.6	80	3	430	210	121	360	180	331

(continued)

No.	(C) Cold rolling step	(D) Heat treatment and plating step										
		(D1)			(D2)	(D3)		(D4)				
	Rolling reduction	Average heating speed of 600°C to max. heating temp.	Max. heating temp.	Value of formula (4)	Holding time	Plating bath dipping-gas wiping time	Steel sheet temp. after gas wiping	Cooling temp.	Ms-cooling temp.	Reheating temp.	Holding time	Ms
	%	°C/s	°C		sec	sec	°C	°C	°C	°C	sec	°C
47	53	1.8	800	-0.6	80	3	420	200	63	380	180	263
48	53	1.7	800	-0.6	80	3	420	60	145	350	180	205
49	53	4.9	880	-0.7	80	3	420	180	163	410	180	343
50	53	3.2	830	-0.6	80	3	430	50	66	370	180	116
51	53	2.1	810	-0.5	80	3	430	230	109	400	180	339
52	53	6.0	910	-0.6	80	3	420	100	117	400	180	217
53	53	2.4	830	-0.6	80	3	420	130	163	370	180	293
54	53	3.1	780	-0.6	80	3	420	170	181	330	180	351

Underlines indicated outside scope of present invention.

[Table 3-1]

[0079]

Table 3-1

No.	Steel type	Microstructure						Surface			Mechanical properties				Cracking of spot weld	Remarks
		Ferrite	Retained austenite	Tempered martensite	Fresh martensite	Pearlite+ cementite	Bainite	No. density of over 2 μm recessed parts	Max. value of Al conc. of Al rich layer	Si_s/Si_b	TS	El	λ	TS×El×$λ^{0.5}$ ×10^{-3}		
		%	%	%	%	%	%	/100um	mass%		MPa	%	%			
1	A	37	12	20	3	0	28	0.2	3.5	0.77	1008	21.7	32	124	VG	Ex.
2	A	33	15	5	12	0	35	0.2	3.3	0.75	996	22.0	20	98	VG	Ex.
3	A	23	11	39	4	0	23	0.0	3.0	0.88	1057	19.3	40	129	G	Ex.
4	A	40	13	15	5	0	27	0.2	3.6	0.95	994	22.3	28	117	Poor	Comp. ex.
5	A	15	11	43	3	0	28	4.7	3.0	0.71	1123	16.9	41	122	Poor	Comp. ex.
6	A	36	12	16	7	2	27	6.1	3.3	0.56	992	21.1	25	105	Poor	Comp. ex.
7	A	35	14	21	4	0	26	0.0	3.2	0.98	1002	22.2	24	109	Poor	Comp. ex.
8	A	39	13	14	6	0	28	2.8	3.5	0.70	1012	22.0	30	122	Poor	Comp. ex.
9	A	33	12	32	5	0	18	0.0	3.4	0.90	1051	19.8	29	112	G	Ex.
10	A	35	13	17	3	0	32	0.4	3.2	0.98	1023	21.5	31	122	Poor	Comp. ex.
11	B	30	8	39	3	0	20	0.1	4.1	0.80	1035	15.2	40	99	VG	Ex.
12	C	46	16	is	4	0	19	0.0	3.1	0.72	998	23.6	25	118	G	Ex.
13	D	48	8	17	2	0	25	0.2	3.9	0.83	987	22.8	24	110	VG	Ex.
14	E	38	11	25	4	0	22	0.2	3.5	0.75	1026	21.9	31	125	VG	Ex.
15	E	36	11	23	2	0	28	0.0	3.3	0.72	1015	22.8	35	137	VG	Ex.

(continued)

No.	Steel type	Microstructure						Surface			Mechanical properties				Cracking of spot weld	Remarks
		Ferrite	Retained austenite	Tempered martensite	Fresh martensite	Pearlite+ cementite	Bainite	No. density of over 2 μm recessed parts	Max. value of Al conc. of Al rich layer	Si_s/Si_b	TS	El	λ	TS×El×$\lambda^{0.5}$ ×10^{-3}		
		%	%	%	%	%	%	/100um	mass%		MPa	%	%			
16	E	79	0	0	0	21	0	0.4	3.1	0.86	793	23.1	27	95	VG	Comp. ex.
17	E	42	12	21	5	0	20	0.2	1.4	0.74	1009	23.0	27	121	Poor	Comp. ex.
18	E	37	12	28	3	0	20	0.2	1.5	0.77	1033	20.9	28	114	Poor	Comp. ex.
19	E	29	13	19	3	0	36	0.2	3.1	0.98	1017	22.5	33	131	Poor	Comp. ex.
20	E	35	3	24	16	0	22	0.1	3.3	0.74	1203	15.2	22	86	VG	Comp. ex.
21	E	32	6	0	41	0	21	0.2	3.3	0.75	1311	14.7	16	77	VG	Comp. ex.
22	E	36	8	20	19	0	17	0.1	3.8	0.79	1128	17.5	20	88	VG	Comp. ex.
23	F	28	10	16	5	0	41	0.4	3.5	0.74	1004	22.2	29	120	VG	Ex.
24	F	30	9	22	3	0	36	1.4	3.0	0.69	995	22.7	25	113	G	Ex.
25	G	31	10	20	5	0	34	0.5	2.8	0.80	1043	20.5	19	93	G	Ex.
26	H	40	16	13	6	0	25	0.3	3.3	0.70	998	24.8	29	133	G	Ex.
27	I	16	10	63	4	0	7	0.2	3.1	0.77	1279	14.8	34	110	VG	Ex.

Underlines indicated outside scope of present invention.

[Table 3-2]

[0080]

Table 3-2

No.	Steel type	Microstructure						Surface			Mechanical properties				Cracking of spot weld	Remarks
		Ferrite	Retained austenite	Tempered martensite	Fresh martensite	Pearlite+ cementite	Bainite	No. density of over 2 μm recessed parts	Max. value of Al conc. of Al rich layer	Si_s/Si_b	TS	El	λ	TS×El× $\lambda^{0.5}$ ×10^{-3}		
		%	%	%	%	%	%	/100um	mass%		MPa	%	%			
28	J	20	14	54	2	0	10	0.2	3.5	0.65	1201	17.3	42	135	VG	Ex.
29	K	13	7	65	3	0	12	0.4	3.2	0.76	1190	14.2	33	97	VG	Ex.
30	L	0	13	70	6	0	11	0.3	3.7	0.73	1198	14.6	52	126	VG	Ex.
31	M	12	11	57	3	0	17	0.0	3.2	0.75	1206	15.9	43	126	G	Ex.
32	N	15	10	62	2	0	11	0.7	3.4	0.72	1213	16.0	45	130	VG	Ex.
33	N	15	4	53	2	3	20	0.1	3.3	0.76	1117	10.9	36	73	VG	Comp. ex.
34	N	16	4	55	3	3	19	0.1	3.5	0.75	1198	11.6	37	85	VG	Comp. ex.
35	N	16	3	76	2	0	3	0.2	3.4	0.77	1262	9.7	51	87	VG	Comp. ex.
36	N	9	11	58	3	0	19	4.0	3.1	0.69	1235	15.2	33	108	P	Comp. ex.
37	N	20	11	51	2	0	16	0.4	3.3	0.63	1181	16.0	34	110	-	Comp. ex.
38	N	5	9	68	3	0	15	0.0	2.9	1.00	1211	15.7	42	123	P	Comp. ex.
39	N	17	12	59	2	0	10	3.1	2.8	0.65	1199	16.1	37	117	P	Comp. ex.
40	O	19	12	53	3	0	13	0.1	3.4	0.81	1235	15.7	38	120	VG	Ex.
41	P	16	8	73	3	0	0	0.2	3.6	0.80	1196	12.0	50	101	VG	Ex.

(continued)

No.	Steel type	Microstructure						Surface			Mechanical properties				Cracking of spot weld	Remarks
		Ferrite	Retained austenite	Tempered martensite	Fresh martensite	Pearlite+ cementite	Bainite	No. density of over 2 μm recessed parts	Max. value of Al conc. of Al rich layer	Si_s/Si_b	TS	El	λ	TS×El×$\lambda^{0.5}$×10^{-3}		
		%	%	%	%	%	%	/100um	mass%		MPa	%	%			
42	Q	0	14	78	8	0	0	0.5	3.0	0.82	1513	13.4	26	103	G	Ex.
43	R	0	16	78	6	0	0	0.4	3.2	0.79	1482	14.8	24	107	G	Ex.
44	S	0	11	75	6	0	8	0.2	3.1	0.77	1500	11.1	33	96	VG	Ex.
45	T	0	5	86	5	0	4	0.1	3.3	0.84	1496	9.3	45	93	VG	Ex.
46	U	33	4	22	4	0	37	0.2	3.8	0.83	915	17.3	36	95	VG	Comp. ex.
47	V	16	18	41	16	0	9	0.2	3.1	0.75	1288	16.7	16	86	G	Comp. ex.
48	W	35	3	31	3	0	28	0.1	2.7	0.80	996	16.0	29	86	VG	Comp. ex.
49	X	17	16	50	6	0	11	0.2	3.2	0.69	1223	19.5	26	122	P	Comp. ex.
50	Y	60	10	9	0	0	21	0.4	3.3	0.74	813	31.1	30	138	VG	Comp. ex.
51	Z	15	8	59	18	0	0	0.2	3.1	0.80	1235	14.0	10	55	VG	Comp. ex.
52	AA	58	12	15	4	0	11	0.3	2.8	0.81	937	23.6	27	115	VG	Comp. ex.
53	A	33	10	36	1	0	20	3.2	3.4	0.72	1017	21.2	32	122	P	Comp. ex.
54	B	38	8	29	3	0	22	2.7	3.9	0.81	1029	15.4	42	103	P	Comp. ex.

Underlines indicated outside scope of present invention.

[0081] In each of Comparative Examples 4, 10, and 38, the pickling conditions were not controlled to within the predetermined ranges, therefore it is believed the pickling excessively proceeded and the Si poor region right under the interface of the base steel sheet and hot dip galvanized layer was not sufficiently formed. As a result, the value of Si_s /Si_b became higher and cracking occurred in the spot welds. In each of Comparative Examples 5, 8, and 39, the pickling conditions were not controlled to within the predetermined ranges, therefore it is believed the pickling did not sufficiently proceed and the internal oxidation layer was unevenly removed. As a result, the number density of the recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer increased and cracking occurred in the spot welds. In Comparative Example 6, the value of formula (1) was high and therefore internal oxidation excessively proceed, therefore it is believed relief shapes at the steel sheet grew larger after that pickling. As a result, the number density of the recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer increased and cracking occurred in the spot welds. In Comparative Example 7, the value of formula (1) was low and therefore internal oxidation did not sufficiently proceed, therefore it is believed that the Si poor layer right under the internal oxidation layer could not be sufficiently formed. As a result, the value of Si_s /Si_b became higher and cracking occurred in the spot welds. In Comparative Example 16, the maximum heating temperature at the heat treatment and plating step was low, therefore austenite was not sufficiently formed and ferrite ended up being greatly formed and the press-formability was inferior. In Comparative Example 16, the maximum heating temperature was lower than Ac1 (717°C) and no austenite able to transform to martensite remained, therefore in the "Ms-cooling temperature" and "Ms" in Table 2, "-" is shown. In Comparative Example 17, the time until gas wiping after dipping in the plating bath was long, therefore it is believed fracture of the Al rich layer present at the interface of the base steel sheet and hot dip galvanized layer ended up starting and as a result the maximum value of the Al concentration of the Al rich layer fell and cracking occurred in the spot welds. In Comparative Example 18, the temperature of the steel sheet after gas wiping was high, therefore similarly it is believed that the Al rich layer ended up starting to fracture and as a result the maximum value of the Al concentration of the Al rich layer fell and cracking occurred in the spot welds. In Comparative Example 19, the value of formula (4) was low and therefore internal oxidation did not sufficiently proceed, therefore it is believed that the Si poor layer could not be sufficiently formed. As a result, the value of Si_s /Si_b became higher and cracking occurred in the spot welds.

[0082] In Comparative Example 20, the reheating temperature at the heat treatment and/or plating step was low, therefore the desired retained austenite content could not be obtained and the press-formability was inferior. In Comparative Example 21, the cooling temperature at the heat treatment and/or plating step was high, therefore tempered martensite was not formed and the press-formability was inferior. In Comparative Example 22, the holding time at the reheating temperature in the heat treatment and/or plating step was short, therefore the fresh martensite content became high and the press-formability was inferior. In Comparative Example 33, the reheating temperature at the heat treatment and/or plating step was high, therefore the desired retained austenite content could not be obtained and the press-formability was inferior. In Comparative Example 34, the holding time at the reheating temperature at the heat treatment and/or plating step was long, therefore similarly the desired retained austenite content could not be obtained and the press-formability was inferior. In Comparative Example 35, the cooling temperature at the heat treatment and/or plating step was low, therefore nontransformed austenite was excessively decreased and similarly the desired retained austenite content could not be obtained and the press-formability was inferior. In Comparative Example 36, the rolling reduction of the cold rolling was low, therefore the steel sheet surface could not be sufficiently flattened and at the finally obtained hot dip galvanized steel sheet, the number density of recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer increased and as a result cracking occurred in the spot welds. In Comparative Example 37, the value of formula (4) became high and therefore not only did Si, etc., become internally oxidized, but Fe also became oxidized and nonplating ended up occurring. For this reason, Comparative Example 37 was excluded from coverage of evaluation as hot dip galvanized steel sheet. In each of Comparative Examples 46 to 48 and 50 to 52, the chemical composition was not controlled to within a predetermined range, therefore the press-formability was inferior. In Comparative Example 49, the Si content was high, therefore cracking occurred in the spot welds. In each of Comparative Examples 53 and 54, the pickling time was short, therefore it is believed the pickling did not sufficiently proceed and the internal oxidation layer was unevenly removed. As a result, the number density of the recessed parts with depths of more than 2 μm at the interface of the base steel sheet and hot dip galvanized layer increased and cracking occurred in the spot welds.

[0083] In contrast to this, in each of the steel sheets of the invention examples, the TS was 980 MPa or more and $TS \times El \times \lambda^{0.5}/1000$ was 90 or more and, furthermore, the test results of the LME cracking resistance of the spot welds were excellent, therefore it was learned that the press-formability and LME cracking resistance of the spot welds are excellent.

Claims

1. A hot dip galvanized steel sheet comprising a base steel sheet and a hot dip galvanized layer formed on at least one surface of the base steel sheet, wherein the base steel sheet has a chemical composition comprising, by mass%,

C: 0.15 to 0.30%,
Si: 0.30 to 2.50%,
Mn: 1.40 to 3.49%,
P: 0.050% or less,
S: 0.0100% or less,
Al: 0.001 to 1.50%,
N: 0.0100% or less,
O: 0.0100% or less,
Cr: 0 to 1.00%,
Mo: 0 to 1.00%,
Cu: 0 to 1.00%,
Ni: 0 to 1.00%,
Co: 0 to 1.00%,
W: 0 to 1.00%,
Sn: 0 to 1.00%,
Sb: 0 to 0.50%,
Nb: 0 to 0.200%,
Ti: 0 to 0.200%,
V: 0 to 1.00%,
B: 0 to 0.0050%,
Ca: 0 to 0.0100%,
Mg: 0 to 0.0100%,
Ce: 0 to 0.0150%,
Zr: 0 to 0.0100%,
La: 0 to 0.0150%,
Hf: 0 to 0.0100%,
Bi: 0 to 0.0100%,
REM other than Ce and La: 0 to 0.0100% and
balance: Fe and impurities, and
a steel microstructure in a range of 1/8 thickness to 3/8 thickness centered on 1/4 thickness from the surface of the base steel sheet comprising, by vol%,
ferrite: 0 to 50%,
tempered martensite: 1% or more,
retained austenite: 5% or more,
fresh martensite: 0 to 15%,
total of pearlite and cementite: 0 to 5%, and
balance: bainite,
when measuring the hot dip galvanized steel sheet by a high frequency glow discharge optical emission spectrometer (GDS), a maximum value of Al concentration of an Al rich layer present at an interface of the base steel sheet and the hot dip galvanized layer is 2.0 mass% or more and an Si_s /Si_b at the base steel sheet right under the interface of the base steel sheet and the hot dip galvanized layer is 0.90 or less,
a number density of recessed parts with a depth of more than 2 μm at the interface of the base steel sheet and the hot dip galvanized layer is 2.0/100 μm or less per interface length, and
a tensile strength is 980 MPa or more, where
Si_s : local minimum value of Si emission intensity at base steel sheet right under interface of base steel sheet and hot dip galvanized layer
Si_b : average value of Si emission intensity at base steel sheet.

2. The hot dip galvanized steel sheet according to claim 1, wherein the chemical composition comprises, by mass%,

Si: 0.30 to 1.20% and
Al: 0.30 to 1.50%.

3. A method for producing the hot dip galvanized steel sheet according to claim 1 or 2, comprising

(A) a hot rolling step including hot rolling a slab having the chemical composition according to claim 1 or 2, then coiling and cooling the obtained hot rolled steel sheet, wherein the cooling satisfies the following formula (1):
[Mathematical 1]

$$0.05 < \sqrt{2 \cdot \sum_{t=0}^{tf} \left(\frac{Do \cdot No}{N_x} \cdot \Delta t \right)} < 1.50 \quad \cdots (1)$$

where,
[Mathematical 2]

$$D_o = 2.9 \cdot 10^{-7} \cdot exp\left(-\frac{90,000}{8.314 \cdot T(t)} \right) \quad \cdots (2)$$

[Mathematical 3]

$$N_o = 0.381 \cdot exp\left(-\frac{104,000}{8.314 \cdot T(t)} \right) \quad \cdots (3)$$

T(t): steel sheet temperature (K) after elapse of "t" seconds from coiling
tf: time (s) until steel sheet temperature reaches 673K
Nx: total of atomic percents (-) of Si, Mn, and Al in steel

(B) a pickling step including applying at least one bending/unbending deformation to the hot rolled steel sheet, then running the hot rolled steel sheet through a temperature 70 to 90°C aqueous solution containing 1.0 to 5.0 mol/L of HCl, less than 3.0 mol/L of Fe^{2+}, and less than 0.10 mol/L of Fe^{3+} by an average speed of 10 m/min or more as pickling treatment for 30 seconds or more,
(C) a cold rolling step of cold rolling the hot rolled steel sheet after the pickling treatment by a rolling reduction of 30 to 75%,
(D) a heat treatment and plating step including heat treating and plating the obtained cold rolled steel sheet, wherein the heat treatment and plating step satisfies the conditions of the following (D1) to (D4)

(D1) heating the cold rolled steel sheet to give an average heating speed from 600°C to an Ac1+30°C to 950°C maximum heating temperature of 0.2 to 20°C/s, wherein an atmosphere around the cold rolled steel sheet satisfies the following formula (4):
[Mathematical 4]

$$-1.0 < \log\left(\frac{pH_2O}{pH_2} \right) < -0.1 \quad \cdots (4)$$

pH_2O: steam partial pressure
pH_2 : hydrogen partial pressure

(D2) holding the cold rolled steel sheet at the maximum heating temperature for 1 to 1000 seconds,
(D3) the time after dipping in the plating bath until gas wiping is 0.1 to 5 seconds and the steel sheet temperature after gas wiping is 440°C or less, and
(D4) cooling the steel sheet to a range of Ms to Ms-200°C, then reheating to a temperature region of 300 to 420°C and holding at the temperature region for 100 to 600 seconds.

Fig. 1

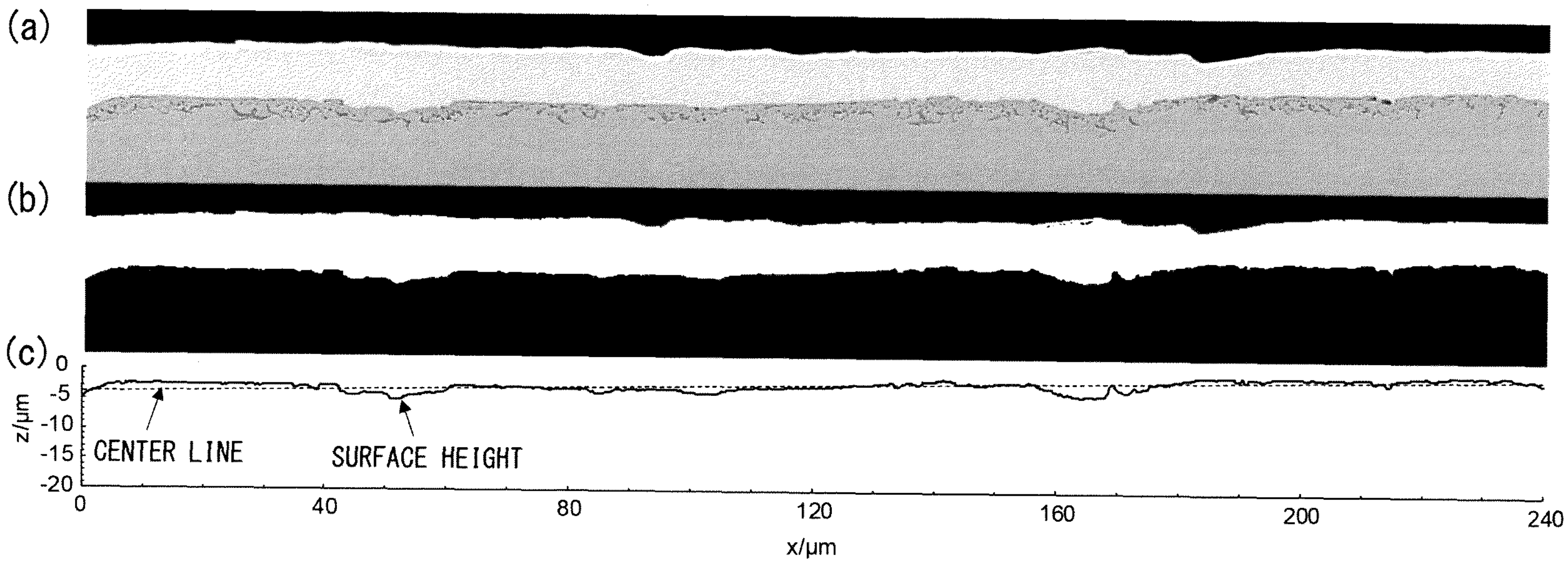

(a)
(b)
(c)
0
-5
-10
-15
-20
z/μm
CENTER LINE
SURFACE HEIGHT
0
40
80
120
160
200
240
x/μm

Fig. 2

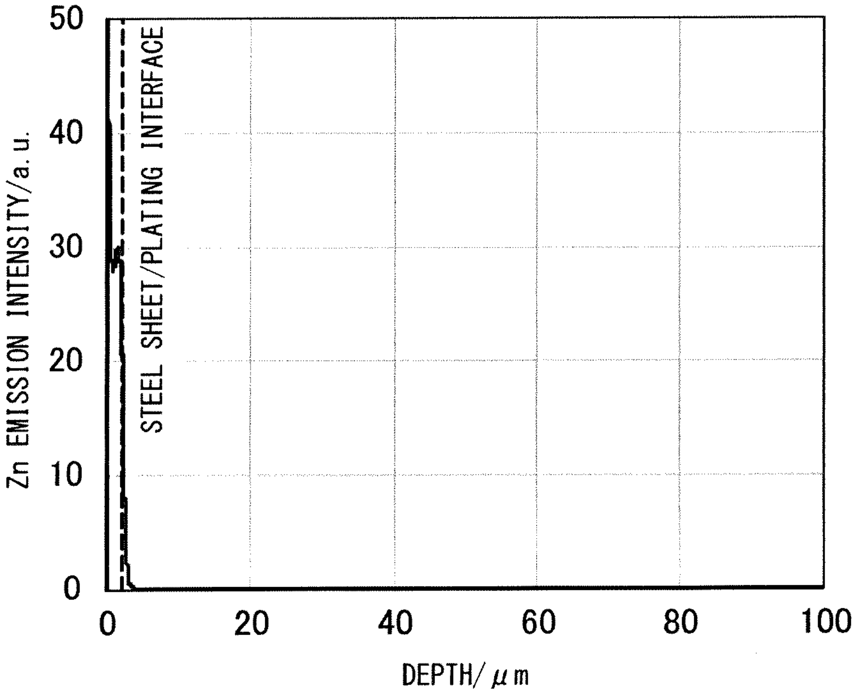

50
40
30
20
10
0
Zn EMISSION INTENSITY/a. u.
STEEL SHEET/PLATING INTERFACE
0
20
40
60
80
100
DEPTH/μm

Fig. 3

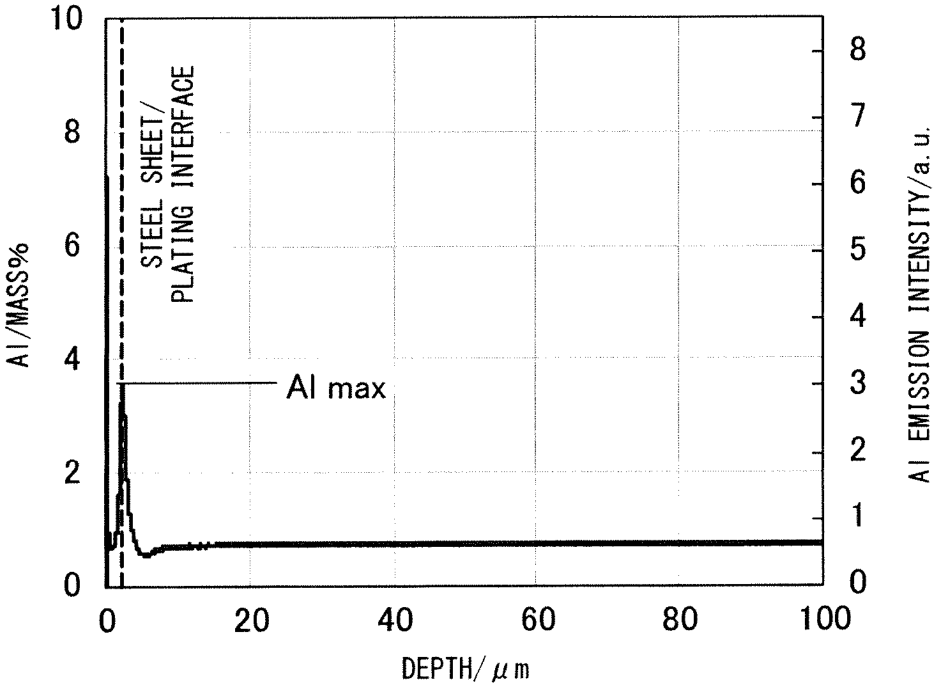
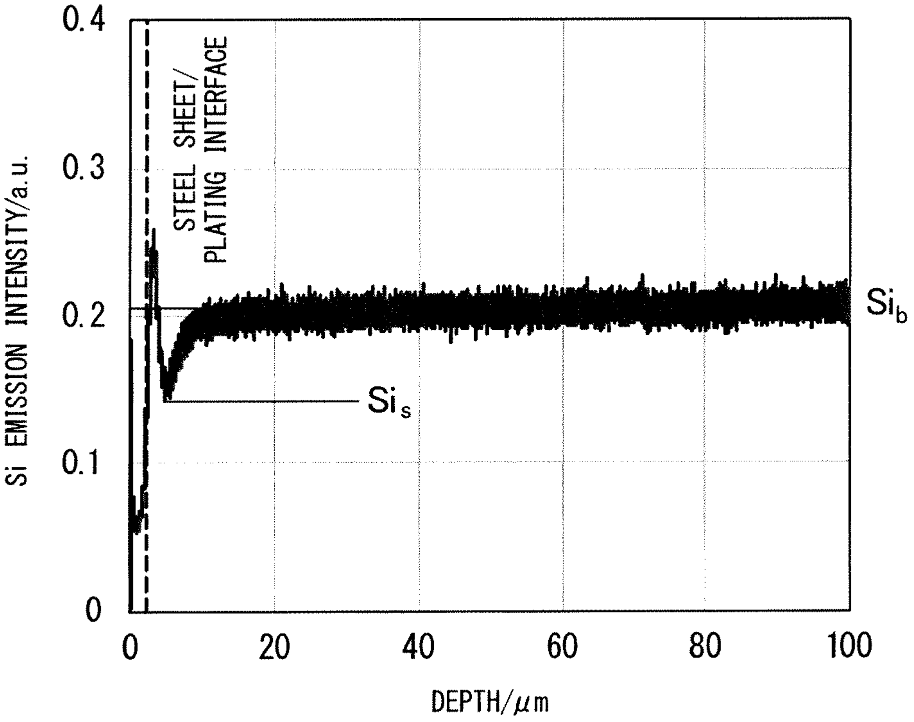

10
8
6
4
2
0
Al/MASS%
STEEL SHEET/
PLATING INTERFACE
Al max
8
7
6
5
4
3
2
1
0
Al EMISSION INTENSITY/a. u.
0
20
40
60
80
100
DEPTH/μm

Fig. 4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0.3
0.2
0.1
0
Si EMISSION INTENSITY/a.u.
STEEL SHEET/
PLATING INTERFACE
Si_b
Si_s
0
20
40
60
80
100
DEPTH/μm

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2022/043968

A. CLASSIFICATION OF SUBJECT MATTER

C21D 9/46(2006.01)i; ***C22C 38/00***(2006.01)i; ***C22C 38/60***(2006.01)i; ***C23C 2/06***(2006.01)i; ***C23C 2/20***(2006.01)i; ***C23C 2/26***(2006.01)i; ***C23C 2/40***(2006.01)i
FI: C22C38/00 301T; C22C38/60; C21D9/46 J; C23C2/06; C23C2/20; C23C2/40; C23C2/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21D9/46; C22C38/00-38/60; C23C2/06; C23C2/20; C23C2/26; C23C2/40

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2023
Registered utility model specifications of Japan 1996-2023
Published registered utility model applications of Japan 1994-2023

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2020/162560 A1 (NIPPON STEEL CORP.) 13 August 2020 (2020-08-13) entire text, all drawings	1-3
A	WO 2020/196060 A1 (NIPPON STEEL CORP.) 01 October 2020 (2020-10-01) entire text	1-3
A	WO 2021/193632 A1 (NIPPON STEEL CORP.) 30 September 2021 (2021-09-30) entire text, all drawings	1-3
A	WO 2016/111272 A1 (KOBE STEEL, LTD.) 14 July 2016 (2016-07-14) entire text, all drawings	1-3
A	WO 2013/047812 A1 (NIPPON STEEL & SUMITOMO METAL CORP.) 04 April 2013 (2013-04-04) entire text, all drawings	1-3
P, A	WO 2022/102218 A1 (NIPPON STEEL CORP.) 19 May 2022 (2022-05-19) entire text	1–3

☐ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search **11 January 2023**	Date of mailing of the international search report **24 January 2023**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/043968

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